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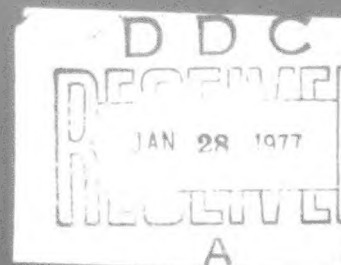
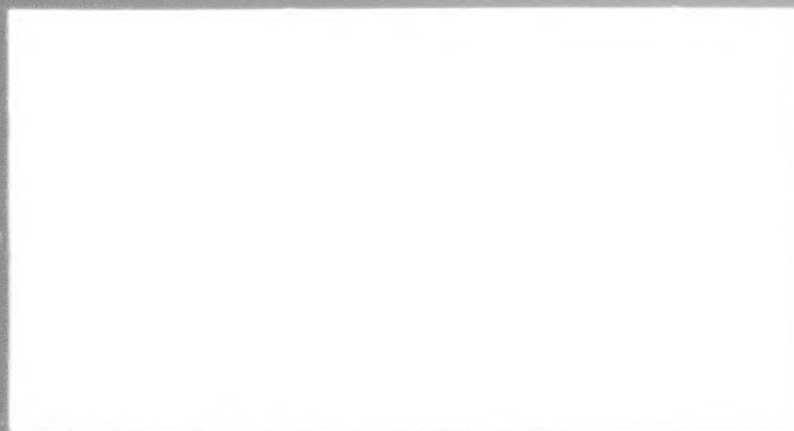
**SIXTEENTH ANNUAL TECHNICAL REPORT,
1 JUNE 1975 TO 31 MAY 1976**

**PENNSYLVANIA UNIVERSITY
PHILADELPHIA, PENNSYLVANIA**

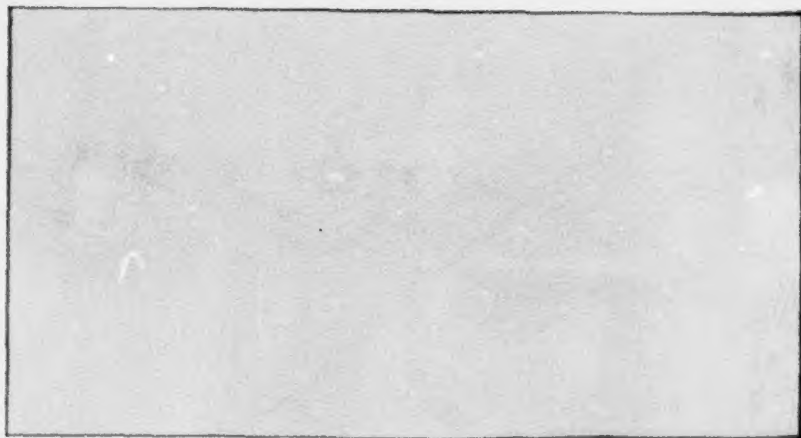
1976

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LABORATORY FOR RESEARCH
ON THE STRUCTURE OF MATTER



UNIVERSITY of PENNSYLVANIA
PHILADELPHIA, PENNSYLVANIA 19174



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report contains information on research programs at the Laboratory for Research on the Structure of Matter at the University of Pennsylvania including programs supported by ARPA and monitored by AFOSR. The major research areas are: Surfaces and Interfaces, Materials Failure Criteria, Molecular Crystals, Chemical and Extractive Metallurgy, and Electronic and Magnetic Materials. The Surfaces and Interfaces Area is involved with the under - standing, on a microscope level, of the bonding of and the interaction		

Block 20 ABSTRACT (Continuation)

between absorbed species on a solid surface. The Materials Failure Criteria Area is concerned with an investigation of the effect of impurities on the fracture behavior of structured alloys, and specifically with the phenomenon of temper embrittlement. The Molecular Crystals Area deals mainly with the preparation and study of materials exhibiting novel solid state properties and with the understanding of chemical design and synthesis procedures which will allow the achievement of desired solid state properties. The Chemical and Extractive Metallurgy Area is an applied science area concerned with the efficient production and conservation of metals with the major objectives of increasing basic knowledge in those areas of high-temperature chemistry which are important for technological advances in extractive metallurgical processes. The Electronic and Magnetic Materials Areas involved with both graphite intercalated compounds and with amorphous magnetic materials.

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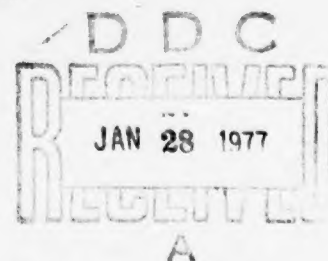
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(Alan J. Heeger, Principal Investigator)



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I. INTRODUCTION

The Laboratory for Research on the Structure of Matter (LRSM) is the official name applied by the University of Pennsylvania to its Materials Research Laboratory, an interdisciplinary research and educational program in the materials sciences, and to the building in which most of the work is done. Operating with a total budget of about 5.1 million dollars, the LRSM program has the active participation of about 44 faculty members, 55 post-doctoral fellows, 118 graduate students, and 35 full-time professional, technical, administrative, and clerical personnel. Approximately 200 scientific and technical publications are produced each year. An important part of the program is the operation of 13 Central Facilities, equipped with specialized apparatus and in most cases employing permanent technical staff.

The LRSM at Pennsylvania has become a successful and well-known center for materials research, and is at the forefront of the work in this field. The materials program in the LRSM includes the generation and study of new materials with new and exciting properties; e. g., polymeric sulfur-nitride, $(\text{SN})_x$, the first metallic polymer, amorphous magnetic materials, one-dimensional organic metals, intercalated graphite, etc. In addition and of equal importance, a considerable fraction of the LRSM effort is directed toward improvement of existing materials and materials processing including for example working toward a solution of the important problem of embrittlement of steels, work on chemical and extractive metallurgy, and a major program in surface science. These programs are characterized by a broad based experimental and theoretical approach spanning the disciplines of Physics, Chemistry, Metallurgy, and Electrical and Chemical Engineering. Underlying the entire program is a philosophy of careful and well-characterized materials preparation. The University of Pennsylvania LRSM is broadly known for this emphasis on quality materials and has set a standard for others to follow.

II. THE LRSM THRUST AREAS

The research programs in the LRSM fall generally into five major Thrust Areas:

1. Surfaces and Interfaces
2. Materials Failure Criteria
3. Molecular Crystals
4. Chemical and Extractive Metallurgy
5. Electronic and Magnetic Materials

The implied focusing of the research into coherent thrust areas at the Penn MRL is evolving naturally and at a satisfactory rate. Our view is that a healthy thrust area should have a coherent core consisting of a group of faculty members working toward solution of a common defined problem which is of a scope larger than that traditionally attacked by a single research investigator. A broad approach, typically using a variety of experimental and/or theoretical techniques, is generally involved. Around each of these cores we envision related work which falls into the same thrust area, but which is peripheral to the central core.

A primary concern of the Thrust Area approach to materials research is the combined need for better definition of existing programs toward solution of identified problems and for the development and growth of new problem areas. Thus, some work outside the core program must continue to receive support, since a breadth of interest and avoidance of narrow specialization is necessary to insure the proper future scientific evolution of the program. At present we have four focused thrust areas (Surfaces and Interfaces, Materials Failure Criteria, Molecular Crystals, and Chemical and Extractive Metallurgy). The fifth area, Electronic and Magnetic Materials, has been more diffuse and has traditionally been the origin of new programs (the Surface program and the Molecular Crystals program both originated there). This process is continuing with two new problems having been developed into coherent scientific programs within the past two years. The study of Graphite Intercalation Compounds is approaching the status of a major LRSM thrust area involving faculty from four different departments. Similarly, work on Amorphous Magnetic Materials has made excellent progress using a combination of experimental and theoretical methods.

1. Surfaces and Interfaces

The primary goal of the Surfaces and Interfaces Thrust Area is to develop an understanding, on a microscopic level, of the bonding of and the interaction between adsorbed species on a solid surface. The core of the thrust is directed specifically to questions concerning the interaction of simple molecules, such as H_2 , CO, and C_2 , with metal atoms of the late transition series when these atoms are in a variety of well-characterized surface environments. Such systems are simple enough to be amenable to experimental and theoretical analysis - both of which are imperative if progress is to be made - and at the same time are of considerable current interest in industrial processes.

A variety of experimental and theoretical techniques are being employed by thrust area members. One must study experimentally the structure of the bonding surface, the nature of reacting species, bonding configurations of reactants, the kinetics of the formation of surface species, etc. Theoretical effort must focus on the phenomena themselves as well as on the interpretation of experimental techniques and results.

The core of the surface thrust area involves principal investigators in three departments - Physics, Chemistry, and Metallurgy and Materials Science. This breadth of expertise allows us to investigate the interaction of adsorbates with a single transition metal atom isolated in a metallo-organic complex, with a sharply etched tip having many facets, and with a nearly perfect macroscopic single crystal surface. This range should lead to considerable insight into the effect of metal coordination on chemisorption and catalysis.

The LRSM has created a central facility for surface studies. Specific surface probe techniques available through the facility and the individual faculty members include photoemission (clean surfaces, molecules on surfaces, gas phase angular resolved, etc.), field emission, field-ion microscopy, Auger electron spectroscopy, surface elastic and electromagnetic wave spectroscopy.

2. Materials Failure Criteria

This area is deeply rooted in a major field of technology, and reaches into the disciplines of physical metallurgy, solid state physics, and chemistry for its scientific understanding. The core problem being attacked is the effect of impurities on the fracture behavior of structural alloys, and specifically the phenomenon of temper embrittlement. This

is a long-standing problem encountered in some alloy steels, notably those used in large cross-sections such as turbine shafts and thick-walled pressure vessels. Certain heat treatments, or service at elevated temperatures, can lead to abnormal brittleness and sometimes to catastrophic failures. It is well-established that the effect originates in the collection of certain impurity elements at the grain boundaries; however, the mechanism of the segregation, the reason for the connection between impurity segregation and brittleness, and effective means of controlling the brittleness remain unknown.

The program on embrittlement was formed from the necessity to attack the problem of residual elements in steels from a number of points of view, employing disciplines outside of traditional physical metallurgy. The program has a unified design, worked out in a collaborative way based on research that was being carried out for a number of years within the LRSM.

The core problem can be stated as follows: Elements from Groups IV to VI, when present in alloy steels in trace amounts, tend to become concentrated in grain boundaries, particularly when a steel is heated for prolonged periods in the temperature region of ferrite + carbide stability. The results of this are reduced fracture toughness and increased tendency for cracking when the steel is stressed in aggressive media or at high temperatures.

Recent work at the LRSM by McMahon (MMS) has led to a new idea about the origin of the segregation, and has inspired a major experimental and theoretical program on temper embrittlement and related impurity effects in structural materials. The approaches include conventional physical metallurgy techniques, thermodynamic methods, surface science, and theory; the faculty members working on the project have backgrounds in metallurgy, physics, physical chemistry, and applied physics.

The long range and short range goals are identical: to develop sufficient understanding of impurity effects at grain boundaries to design alloy compositions and heat treatments that will significantly improve the performance of structural materials.

Other efforts falling under the general heading of materials failure criteria include studies of the origin of the mechanical strength of ordered alloys, of the nature and prevention of mechanical damage due to cyclic loading, of phase transformations and mechanical properties of amorphous metals, and the deformation of polymers, emphasizing low-temperature surface effects.

3. Molecular Crystals

This program stands on the border between solid state physics and synthetic organic and inorganic chemistry. It combines the enormous power of chemistry to provide new materials, and the sophistication of solid state physics to measure and interpret electronic properties, in an effort to learn to predict properties and design compounds that would be useful in technology. Success in this area requires active collaboration between physicists and chemists, and we believe we have achieved highly effective cooperation.

In addition to its major activity, preparing and studying new materials exhibiting novel solid state properties, a principal objective is to obtain sufficient fundamental understanding to allow the achievement of desired solid state properties by chemical design and synthesis of the molecular units.

An important part of the research in this area involves a class of solids known as organic charge transfer salts, plus other pseudo-one-dimensional systems which are evolving out of the interdisciplinary program. The short range goal is to prepare and study these materials, especially instabilities in the one-dimensional electron gas which lead to the metal-insulator (Mott) transition, and the Peierls-Fröhlich charge density wave collective state. The long-range goal is to arrive at an understanding of theory and a command of synthesis such that useful technological materials can be predicted, designed, prepared, and put to use. At present attention centers on the synthesis and study of new organic charge transfer salts (analogous to the TCNQ salts), organo-metallic salts, and polymers.

The LRSM has created a central facility for organic crystal growth which is devoted almost entirely to this Thrust Area, and which is functioning very successfully.

The LRSM has in addition a strong and far reaching program on non-metallic molecular crystals. The work is both experimental and theoretical, and a wide range of molecular materials are being synthesized and studied. Of particular interest to this group is the study of the electronic structure and relaxation process in molecular crystals. A new program on laser induced isotope separation is successfully underway.

4. Chemical and Extractive Metallurgy

It has recently been stated that the wealth implicit in American mineral resources is no longer a bonanza which lies in the ground for the

taking - it now lies in the extractive technology employed. Present-day metallurgical extractive and refining technology is rapidly becoming inadequate due to the declining quality of available ores, the demand for recycling of scrap metals, the need for lower impurity levels in refined metals, and the increasingly stringent air and water pollution controls. With rare exceptions, the development of new processes depends upon the discovery of new chemical and process principles.

Deterioration and eventual destruction of materials by reactions with their environment contribute extensively to the depletion of our material resources. From a financial viewpoint, it has been estimated that the total cost of corrosion and corrosion protection in the United States is 8 billion dollars annually. Corrosion-resistant materials are especially needed for high-temperature applications such as gas turbines.

Chemical and Extractive Metallurgy is an applied science concerned with the efficient production and conservation of metals. The major objective of the Chemical and Extractive Metallurgy Thrust Area is to increase basic knowledge in those areas of high-temperature chemistry which are important for technological advances in extractive metallurgical processes and in corrosion-resistant materials. The selection of research projects is strongly influenced by their pertinence to specific technological problems. Current projects are concentrated in five research areas, in which basic studies are needed for future technological advances. These areas are multicomponent metallurgical solutions, interfacial kinetics, new electrochemical sensors, high-temperature corrosion and high-temperature vapor species.

This is a small group, but it is now the largest similar program at any U. S. University. Although a range of topics is under investigation, and the faculty have quite different backgrounds and research specialties, the effort is highly cooperative. The faculty members and students work closely together, and a regular weekly internal seminar is held to present and discuss the progress of current research.

5. Electronic and Magnetic Materials

The two principal programs within this area involve Graphite Intercalation Compounds and Amorphous Magnetic Materials.

The Graphite Intercalation Compound program grew out of the current interest in materials science research directed toward non-three-dimensional materials, in which the transport or optical properties are markedly anisotropic. These studies are motivated by the intrinsic

interest of systems in which carriers are confined to move in limited directions in the crystal, and also by the promise of designing specific characteristics into materials at the atomic or molecular level. The organometallic charge transfer salts, $(\text{SN})_x$, etc. are other related examples in the Penn MRL program.

The anisotropic atomic bonding in graphite produces a layer-type crystal structure which permits the insertion of many different atomic or molecular species between the hexagonal carbon monolayers. The resulting materials possess well-ordered superlattices along the c-axis normal to the layers. Stoichiometric compositions can be synthesized corresponding to isolated monolayers of inserted atoms or molecules with constant area density separated by one or more graphite planes. The number of intervening graphite planes is referred to as the "stage" of the compounds, stage 1 being the fully saturated composition. The inserted species can act as electron donors (e. g., alkali metals) or acceptors (halogens, acids), in some compounds the a-axis conductivity σ_a (parallel to the layers) increasing to values approaching or exceeding that of copper, as discussed below.

The goals of the graphite intercalation program are: 1. to synthesize well-characterized graphite intercalation compounds with room temperature conductivity greater than that of copper; 2. by a close coupling among synthesis, physical measurements and theoretical analyses, to obtain a basic understanding of the chemical and structural effects of intercalation on the electronic structure, to provide the basis for the design of new compounds with specific optimized properties; 3. to develop composite materials which will demonstrate the practical realizability of highly conducting intercalation compounds; and 4. to ascertain the reaction kinetics of intercalation and de-intercalation, thus elucidating the charge transfer reactions and determining the optimum conditions for compound formation.

In magnetic materials, interest centers on amorphous magnetic materials and in particular on magnetic alloys. These materials, made in the form of narrow ribbons by very rapid cooling from the liquid state, have been found to have soft magnetic properties that make them competitive with the best available commercial materials. The research includes the production of new alloys, the measurement of magnetic properties and exploration of ways to improve properties, and an attempt to understand the properties. This program is unusual at the University in that the short-range goal is to make a useful material, and the long-range goal is to understand why and how it works.

III. RESEARCH HIGHLIGHTS, 1975-76

Some significant results of the LRSM research program in 1975-76 are presented here. They are arranged by thrust areas, and the principal contributing faculty are indicated.

1. Surfaces and Interfaces

Angular Resolved Photoemission as a Surface Probe

A prerequisite for understanding surface phenomena is surely an ability to determine the bonding configuration of adsorbed atoms or molecules. This encompasses both geometrical as well as electronic configuration, but it is blatantly clear at this stage of development that the lack of geometrical information is limiting the progress in this field.

Our approach at Penn was to investigate photoemission as a probe of the bonding configuration of atoms or molecules. It is clear that there is a wealth of information contained in the angle and energy resolved emission from a molecule with fixed orientation with respect to the polarization of the light and the orientation of the crystal surface. The problem is that photoemission for molecules on surfaces was not understood in sufficient detail to be a useful tool. The solution of this problem necessitated a large joint theoretical-experimental effort, both on gas phase molecular photoelectron spectroscopy and the equivalent photoelectron spectra of adsorbed molecules.

The first step in this program was to develop a detailed understanding of the photoionization process in the gas phase molecules of interest to the surface program. Experimentally we have measured the frequency dependence of the partial photoionization cross section for some 10-15 molecules and developed a theory capable of quantitatively explaining these cross sections (at present for N_2 , CO and CO_2). This joint effort in itself has led to a detailed understanding of the photoionization process which is a major advance in the field of gas phase photoionization. As a consequence of this understanding, we know the angular dependent electron emission from a specific orbit of the molecule with a fixed orientation in space as a function of the photon energy and polarization. Knowing this information we can now predict what the angular emission from a molecule on the surface should be for any orientation. The two accompanying figures illustrate these capabilities for CO adsorbed on Ni (100). They represent two of the most straightforward types of experiments possible.

In Fig. 1 we show the calculated intensity from the 1π orbital of CO for both a standing-up and lying-down orientation. The 1π orbital can only be excited by an electric field perpendicular to the molecular axis, so in Fig. 1 we have plotted the emission normal to the surface as a function of the angle of incidence of the light, using the Fresnel's equations to calculate the direction and strength of the electromagnetic field at the surface. The X's are the experimental points which have been normalized to the appropriate curves. Figure 2 illustrates another simple experiment where the light is held at normal incidence and the angular dependence of the emission from the 1π orbital is measured. Again the two calculated curves are for CO standing-up and lying-down and the X's are the experimental data. Comparison of theory and experiment clearly demonstrates that CO bonds to the Ni surface in the standing-up configuration.

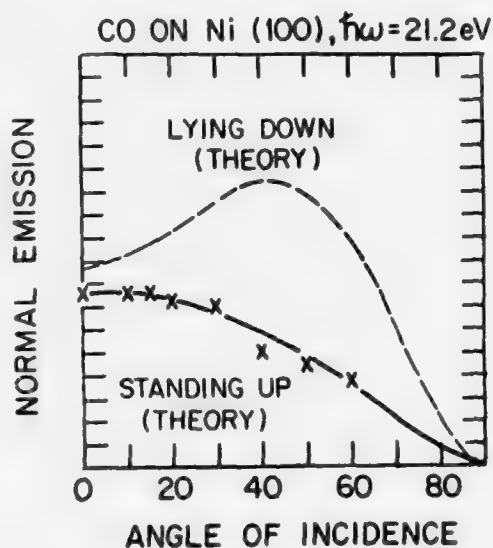


Fig. 1 Theoretical predictions and experimental data (X's) for the normal emission (from the surface) from the 1π orbital of CO as a function of the angle of incidence of the incident radiation. The solid theoretical curve is for CO standing-up and the dashed curve is for CO lying-down. The experimental data is normalized to the standing-up curve at normal incidence.

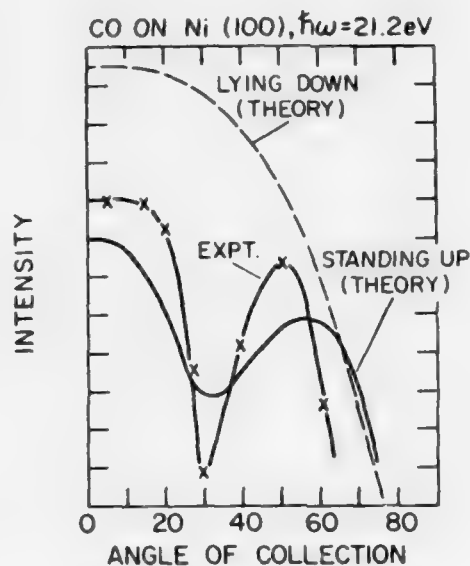


Fig. 2 Theoretical prediction and experimental data (X's) for the angle of emission from the 1π orbit of CO. The solid curve is the theoretical prediction for a standing-up molecule and the dashed curve is for a lying-down molecule. The data has an arbitrary normalization factor.

These experiments, which are being extended to more complex angular configurations and to various photon energies, will allow us to map out the spatial configurations of each orbit as well as determining the bonding geometry.

This work was carried out in a joint experimental-theoretical effort directed by Profs. Schrieffer, Soven, Plummer, and Gustafsson.

2. Materials Failure Criteria: Embrittlement of Alloy Steels

A major program on embrittlement of alloy steels has developed within the LRSM. Based on the important initial accomplishments of Profs. McMahon and Pope on the role of critical impurities in the embrittlement process a broad based study is underway.

Understanding of the mechanisms of impurity-induced intergranular embrittlement of steels continues to expand. Last year we reported that: (1) the three primary variables: intergranular concentration and potency of metalloid impurities, hardness, and grain size had been isolated and studied, (2) it was established that temper

embrittlement involves equilibrium co-segregation of metalloid impurities and certain alloy elements (e. g. Ni and Mn), and (3) certain alloy elements could precipitate specific metalloids and thus eliminate embrittlement (e. g. Ti + P, Mo + P). We have now found that there are additional roles for alloy elements. For example, Cr enhances the segregation of Ni + Sb, and Ni + P to grain boundaries; the thermodynamics of this interaction are still under study. Furthermore, the presence of certain alloy elements in grain boundaries can reduce the embrittling potency of metalloids (e. g. Ti + Sb). There is now reason to believe that others can enhance the embrittling potency (e. g. Ni or Cu). These latter effects presumably carry information about the physics of embrittlement which is now under study. The factors being considered are: charge transfer from electron-rich metalloid elements to the Fe d-band, the effects of substitutional metallic solutes with relatively empty d-bands (e. g. Ti) or full d-bands (e. g. Cu or Ni), and the effects of increase or decrease in atomic volume due to misfitting metalloids.

The prior heat treatment of $2\frac{1}{4}\text{Cr}-1\text{Mo}$ steel, commonly used in high temperature applications, has been found to play an important role in determining the degree of embrittlement during subsequent exposure to lower temperatures. This has to do with the amount of Mo_2C precipitation which has taken place, since Mo is an important metalloid scavenger but is ineffective if tied up as a carbide.

The overall program on intergranular embrittlement is now approaching the desired level of activity. We have underway simultaneous studies of one-step and two-step temper embrittlement, effects of metalloids on creep rupture behavior and on stress relief cracking in pressure vessel and high temperature structural steels, and effects of H_2 and aqueous environments on crack growth in pressure vessel steels. The efforts in the area of true stress corrosion cracking (involving intergranular anodic dissolution rather than H_2 effects) are just getting underway. MRL funding has continued to provide the stabilizing matrix for this work. A substantial block of the work is now funded by EPRI, with lesser portions by AISI, NSF (Division of Materials Research), MPC, and Naval Air Systems Command.

In summary the transformation to a large, parallel-path attack on this generic problem area is almost complete and has already started to bear fruit at a greatly increased rate.

3. Molecular Crystals

A. Electrical Conductivity of $(\text{SN})_x$

Polymeric sulfur nitride, $(\text{SN})_x$, also known as polythiazyl, is the only known example of a metallic polymer and is believed to be the first member of an entirely new class of materials referred to as polymeric metals. In single crystal form, $(\text{SN})_x$ exhibits an anisotropic electrical conductivity with a metal-like temperature dependence as well as optical properties which are similarly anisotropic and metal-like. The normal state transport properties of $(\text{SN})_x$ continue to be important in understanding the electronic properties of this novel system.

We have studied the temperature dependent conductivity along the \underline{b} axis of many $(\text{SN})_x$ crystals as a function of polymerization time. A general increase in the conductivity with longer polymerization times was found, leading to room temperature conductivities from 1200 - 3700 $(\Omega\text{-cm})^{-1}$ and resistivity ratios exceeding 200. The results for the temperature dependence of the resistivity can be expressed in terms of Matthiessen's rule traditional for ordinary metals. The resulting temperature dependent term can be represented accurately by a simple T^2 form over the broad temperature range 15 through 250 K, independent of sample polymerization time.

Recently on the basis of x-ray crystallographic results for S_2N_2 , partially polymerized S_2N_2 , and $(\text{SN})_x$, we have investigated the experimental conditions and reaction mechanism for the solid state polymerization of S_2N_2 to $(\text{SN})_x$. Since the transport mean free path is expected to increase with polymer perfection and chain length, one expects that analytical purity and relatively long polymerization time in forming $(\text{SN})_x$ from S_2N_2 would lead to fewer impurity and defect scattering centers. Having developed techniques for attaining analytically pure material, the solid state polymerization of S_2N_2 was carried out at room temperature for 3 days, 4 weeks and 10 weeks. The initial results given in Figure 3 show that the observed maximum conductivity $\sigma_M^b(T) / \sigma^b(300\text{ K})$ measured parallel to the polymer chain direction exhibits a general overall increase with longer polymerization times. Since the measured samples have equally high purity, fewer defects apparently occur in an average $(\text{SN})_x$ chain with increased polymerization time.

The normalized \underline{b} -axis conductivity $\sigma^b(T) / \sigma^b(300\text{ K})$ as a function of temperature for seven representative samples is shown in Figure 4. Of the seven samples, five were polymerized for 10 weeks, one for 4

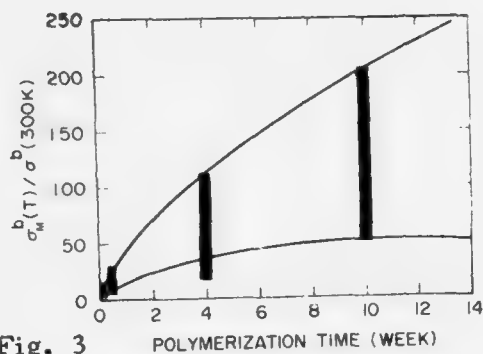


Fig. 3

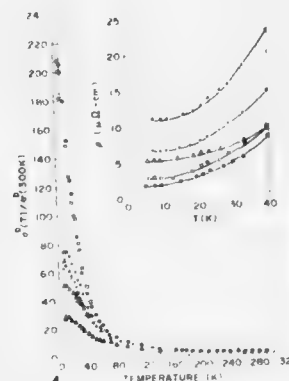


Fig. 4

weeks and one for 3 days. The results show that as the resistance ratio increases, the temperature for the maximum conductivity shifts to lower temperatures, and the conductivity maximum becomes less pronounced. These observations confirm the maximum (resistivity minimum) is due to extrinsic contributions from chain breaks and defects. For the 4 and 10 week samples, the resistivity appears to monotonically approach a low temperature residual value as in ordinary metals (Fig. 4 Insert). The measured conductivity at 5 K in the best sample is $5.5 \times 10^5 (\Omega\text{-cm})^{-1}$.

The temperature dependence of the resistivity can be represented by Matthiessen's rule showing the intrinsic resistivity over a broad temperature range $15 < T < 250$ K follows a T^2 form, which has been attributed to electron-electron scattering between pockets, or sheets, of the Fermi surface separated by approximately half a reciprocal lattice vector.

With regard to the measurement of its solid state properties the chemical stability of $(\text{SN})_x$ is of critical importance. Detailed studies of the chemical stability of pure crystalline $(\text{SN})_x$ towards air, dry oxygen (1 atm. pressure), moist oxygen (1 atm. pressure) and water vapor have been performed. It has been demonstrated conclusively that completely polymerized $(\text{SN})_x$ undergoes no detectable reaction with the above substances during 1 week at room temperature; however, if the $(\text{SN})_x$ contains any unpolymerized monomer, S_2N_2 , the material reacts readily with air.

This study of the control and improvement of the electrical conductivity of $(\text{SN})_x$ represents a combined materials effort within the LRSM. The joint chemical and physical studies of $(\text{SN})_x$ were carried out by Prof. A. G. MacDiarmid (Chem.), Prof. A. F. Garito (Phys.) and Prof. A. J. Heeger (Phys.).

B. Collective Charge Density Wave Phenomena in TTF-TCNQ

We have put considerable effort into the development of a complete experimental understanding of the one-dimensional metal, TTF-TCNQ, to provide a firm basis for the development of a microscopic mechanism. The results of these studies are providing evidence for one dimensional collective phenomena in the coupled electron-phonon system.

Joint Brookhaven-Orsay-Penn studies have provided direct structural evidence of the Peierls instability in TTF-TCNQ as originally proposed by the Penn group more than three years ago.

The x-ray diffuse scattering studies have shown the existence below 54 K of a low temperature 3 D charge-density-wave superlattice having an incommensurate modulation of $3.4 b$ in the chain direction and have provided evidence above 54 K of 1 D diffuse scattering consistent with a lattice distortion or phonon anomaly. Subsequent elastic neutron studies revealed below 38 K the 3 D modulated lattice, $4 a \times 3.4 b \times c$, undergoes a change at 38 K in which the transverse a modulation varies continuously from $4 \bar{a}$ to a value of $2 \bar{a}$ at 47 K. From 47 to 54 K, the modulated lattice remains $2 \bar{a} \times 3.4 \bar{b} \times \bar{c}$, and above 54 K the modulated lattice structure disappears. Thus, TTF-TCNQ exhibits three structural transformations at 54, 47 and 38 K, respectively. In the metallic state, inelastic neutron scattering studies have revealed a $2 k_F$ Kohn anomaly located at $0.295 \bar{b}^*$ at room temperature which in deuterated samples becomes stronger with decreasing temperature. The corresponding 1 D diffuse scattering streaks (1 D lines modulated by the molecular form factors) show up clearly in the x-ray patterns above 54 K.

These results, together with the observations of the energy gap and the extremely narrow zero frequency mode in $\sigma_1^b(\omega)$ as obtained from dc, microwave, IR and optical studies show that TTF-TCNQ is not a simple metal and that collective effects are dominant features of the electronic properties.

The reflectance studies on single crystal mosaic samples of TTF-TCNQ have been extended into the far infra-red (12 cm^{-1} to 100 cm^{-1}) in both the conducting and insulating regimes. The results confirm the existence of the energy gap at all temperatures and provide information on the distribution of low frequency oscillator strength. The results of these far-IR studies of $\sigma_1(\omega)$ at 100 K are shown in Fig. 5. The dc and microwave data for typical samples are included in the figure.

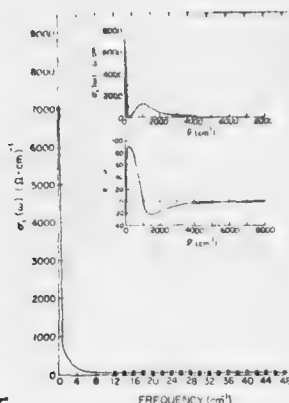


Fig. 5

The full frequency dependence of $\sigma_1^b(\omega)$ (Fig. 3) shows a maximum at 1000 cm^{-1} with a smooth, Drude-like frequency dependence observed at higher frequencies. The corresponding behavior of $\epsilon_1^b(\omega)$ (Fig. 5) is like that of a semiconductor with a transition across the energy gap sufficiently strong to give negative values between 1000 and 6000 cm^{-1} . At lower frequencies ϵ_1^b is positive with magnitude of approximately 100; consistent with the measured oscillator strength across the gap (0.14 eV) as obtained from the plasma frequency (1.2 eV); $\epsilon \approx 1 + \omega_p^2 / \omega_g^2 \approx 100$. The large zero frequency conductivity drives ϵ_1^b negative in the far IR.

The energy gap remains as the dominant feature in $\sigma_1(\omega)$ and $\epsilon_1(\omega)$ in the insulating state at 4.2 K . Measurements of the \underline{b} -axis reflectance in the gap region below 50 cm^{-1} reveal an optical mode centered at approximately 2 cm^{-1} , suggesting that the oscillator strength responsible for the conductivity above 54 K is shifted to finite frequency in the insulating state. The large low temperature dielectric constant, $\epsilon_1^b = 3500$, is quantitatively consistent with the low temperature far IR observations.

The experimental behavior of TTF-TCNQ is currently being pictured in terms of the phenomenological model of a Peierls-Fröhlich condensation of the conduction electrons with a high mean field scale temperature. In this model, the electronic properties are dominated by charge density wave (CDW) fluctuations associated with the Peierls instability in which a phonon mode is driven soft by the divergent response function of the 1D electron gas at $q = 2k_F$. The Peierls instability thus would lead to the metal-insulator transition near 54 K and the periodic superlattice distortion in the low temperature semiconducting state. Above 54 K , in the fluctuation regime, the observed

energy gap (0.14 eV) is identified as the Peierls gap with the condensate moving to contribute to the high dc and microwave conductivity. Below 54 K, the condensate is pinned by high order commensurability, inter-chain coupling or defects leading to the observed incommensurate superlattice and to a shift of the collective mode oscillator strength into the IR with an associated conversion of the dc conductivity into the large low frequency dielectric constant as observed experimentally.

The observation of the incommensurate superlattice is of fundamental importance, for it implies that the phase of the distortion is arbitrary and only becomes fixed by higher order effects or the relatively weak interchain coupling. As a result, so long as

$$k_B T > (\zeta(T)/b) V_0(\varphi)$$

where $\zeta(T)$ is the longitudinal coherence length, b the lattice constant, and $V_0(\varphi)$ the amplitude of the periodic pinning potential, the fluctuating charge density wave can move to form a current carrying state.

Due to the lack of long range order and the presence of intrinsic dissipative processes, persistent currents are not expected, and thus a Peierls-Fröhlich condensate is not a superconductor. However, the extremely weak pinning forces (ω_{pin} of order a few wavenumbers) observed in TTF-TCNQ and the corresponding weak interchain coupling suggest the possibility that under proper conditions the pinning might be suppressed leading to a wider fluctuation range and higher conductivity.

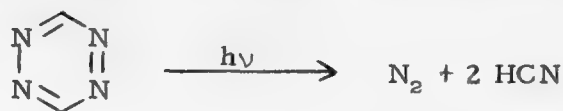
A broken symmetry conduction mechanism arising from a (nearly) phase independent charge density wave would represent the only example yet found in nature of collective electron transport which is different from pairing superconductivity. The experimental evidence for collective transport in these 1D materials is accumulating and is a principal reason for their interest.

C. Isotope Separation in Molecular Crystals

The separation of rare isotopes is an outstanding materials problem of the seventies. Currently a number of groups in the US, Israel and the USSR are employing lasers to induce isotope separation in small molecules in moderately low pressure gases. In the MRL program at Pennsylvania a group consisting of Hochstrasser and Smith is developing new approaches to the separation of isotope. This program is an interdisciplinary effort of an organic (Smith, Chem.) and a physical (Hochstrasser, Chem.) chemist which combines expertise in modern

laser technology and in the design and synthesis of molecular materials having electronic and photochemical properties suitable for isotopically selective chemistry. In a particular innovation, an essentially complete isotope separation for carbon-13, nitrogen-15 and deuterium from natural abundance has recently been completed by utilizing an organic solid (s-tetrazine) as the active material. This result is typical of what the group is trying to do; namely to bring about very efficient isotope separation by capitalizing on their insight into the design, synthesis and light induced reactions of molecules.

As one example of our accomplishments in this area, we describe the laser induced separation of D, ^{13}C and ^{15}N employing the material, s-tetrazine. Figure 6 displays a dye laser fluorescence spectrum of the first singlet of this azine dispersed in a benzene crystal at 1.6 K. The weak sidebands correspond to molecules containing either D, ^{13}C and ^{15}N as indicated. (Isotopically substituted molecules can be spectrally resolved in other mixed crystals as well.) In addition, we have learned that in condensed phase at these temperatures s-tetrazine undergoes a rapid novel photochemical dissociation to nitrogen and HCN. Thus by



employing selected narrow band ($\sim 0.8 \text{ cm}^{-1}$) tunable dye laser irradiation it has been possible to produce HCN and N_2 having known isotopic compositions.

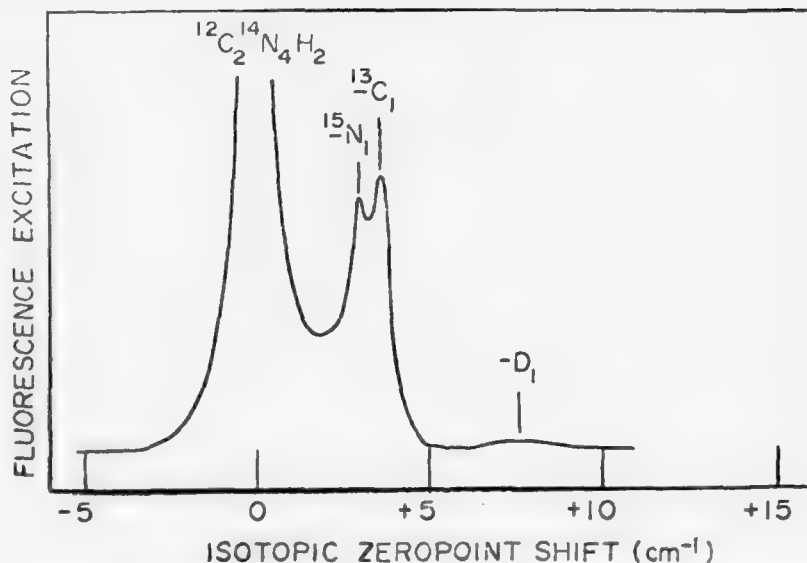
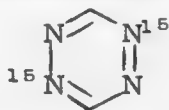


Fig. 6

Samples of s-tetrazine dispersed in a benzene crystal at 1.6 K were irradiated at a specific transition. The respective excitation spectra of the photolyzed samples demonstrate the high degree of isotopic selectivity achieved in the decomposition reaction.

To explore the mechanism of this novel photochemical reaction as well as the high resolution spectroscopy of s-tetrazine, we have prepared the specifically labeled s-tetrazine- $^{15}\text{N}_2$.



Irradiation of this material leads again as expected to the formation of two equivalents of HCN and one equivalent of N_2 . Interestingly only nitrogen of molecular weight 29 ($\geq 97\%$) was formed thus demonstrating that the mechanism of the photochemical decomposition does not proceed via a "dewar benzene" like intermediate.

4. Chemical and Extractive Metallurgy

Mass Spectrometric Studies of the Thermodynamics of Mixing Molten Silicates

An understanding of the factors which influence the thermodynamics of mixing in molten silicates is important in seeking to control and influence the distribution of metals and non-metals between a metal phase and a slag phase in extraction and refining processes. A collaborative effort within the Chemical and Extractive Metallurgy program in the LRSM has resulted in important progress in this area.

The determination of the activity of a single component in a slag system at a few compositions is itself often a lengthy research project. Prof. D. R. Gaskell has been studying the thermodynamics of mixing (and other physical properties) in a number of molten silicates to investigate the effects of ionic size and oxygen coordination number of the components. The very ionic alkali silicates were considered to be the most suitable systems for the near isolation of ionic size effects, but none of the traditional methods were useable for the determination of the thermodynamics of mixing of, for example, the sodium and potassium silicates. Knudsen cell-mass spectrometric methods for the determination of activities and free energies of mixing in binary and multi-component metallic solutions had previously been developed by Prof. G. R. Belton. A collaborative effort was undertaken to see if modification of these methods could lead to suitable techniques for the mixed alkali silicates.

This joint program has been successful. Measurements of the virtual equilibrium



have been used to derive the thermodynamic properties of these melts. A particularly useful attribute of the method is that the effects of foreign cations on the mixing properties can be readily followed since the mass-spectrometric method is specific, i. e., vapor species other than those of interest do not interfere in the measurement.

An example of the results is shown in Figure 7, where the remarkable effect of a relatively small addition of CaO is shown. The excess free energy of mixing of the metasilicates per mole of alkali cations is essentially halved by this addition. This "compensation" effect is consistent with cation size effects being the principal cause of positive deviations from ideal silicate mixing in these strongly ionic silicate systems. The effect on the excess free energies and thus the mixing demonstrated in the figure represents an important step toward better control of extraction and refining processes.

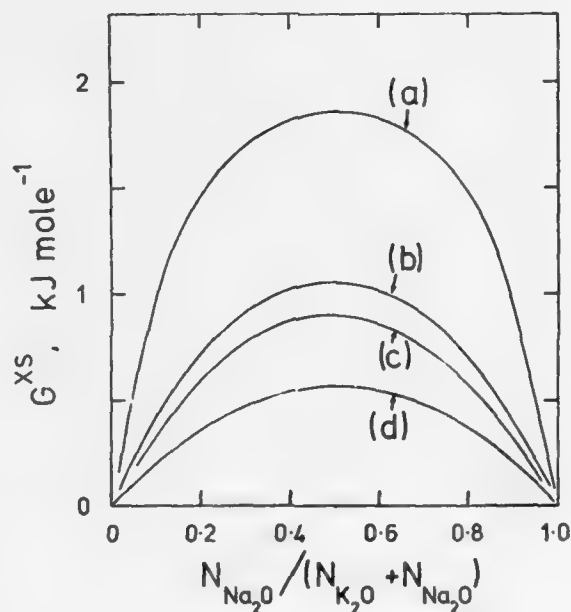


Fig. 7

Excess free energies of mixing of the pseudo-binary constituents per mole of alkali cations at 1100°C.
(a), metasilicate; (b), metasilicate containing Ca);
(c), disilicate; (d), tetrasilicate.

5. Electronic and Magnetic Materials

A. Graphite Intercalation Compounds: A New Class of Synthetic Metals

The study of graphite intercalation compounds is motivated by the fascinating chemical and physical properties as a function of intercalated specie and concentration, and by their potential for application as synthetic electrical conductors and catalysts. The graphite intercalation program within the LRSM is evolving as an interplay among chemical synthesis, physical measurements and theoretical studies, involving faculty from EES, MMS and CBE Departments. The eventual goals of the program are to optimize the material properties through a broad interdisciplinary approach, and thereby to devise composite materials which will lead to practical realization of synthetic conductors based on intercalation compounds.

Figure 8 shows a crystal structure typical of alkali metal compounds of the general formula MC_g , $M = K, Rb, Cs$. This is a first stage compound, that is, a monolayer of metal atoms separates every pair of nearest neighbor graphite monolayers. Dilute stoichiometric compositions can also be made with n contiguous graphite layers, $n \geq 2$. The emphasis of our program to date has been on compounds intercalated with strong acids: HNO_3 , BF_3 , SbF_5 and $SbF_5 + HF$. The working hypothesis is that the stronger the oxidizing power of the intercalated specie, the greater the electron transfer from carbon atom to acid molecule, resulting in a larger free hole density hence higher conductivity.

Figure 9 shows a series of reflectance spectra on strong acid compounds (J. E. Fischer, EES). The minimum in R , characteristic of a classical metal, shifts to higher energy with increasing acid strength, in agreement with the hypothesis. Table 1 presents the a -axis conductivity relative to copper for graphite and several compounds. Scaling the $SbF_5 + HF$ reflectance data to that of HNO_3 allows us to predict that the former compound has a room temperature conductivity 40% greater than that of copper. The prediction is borne out by measurements on partially-aligned compactions of $SbF_5 + HF$ - intercalated powder in Cu tubes; the conductivity of the compacted core is $8 \times 10^5 (\Omega cm)^{-1}$, which is a lower limit due to incomplete alignment of the powder grains and possible interparticle impedances (F. L. Vogel, EES).

The microscopic origin of the conductivity increase (carrier density, mobility, etc.) is being studied using traditional solid state techniques and detailed correlation between chemical composition and

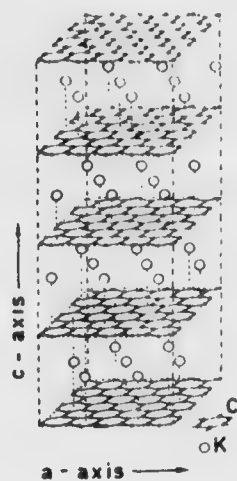
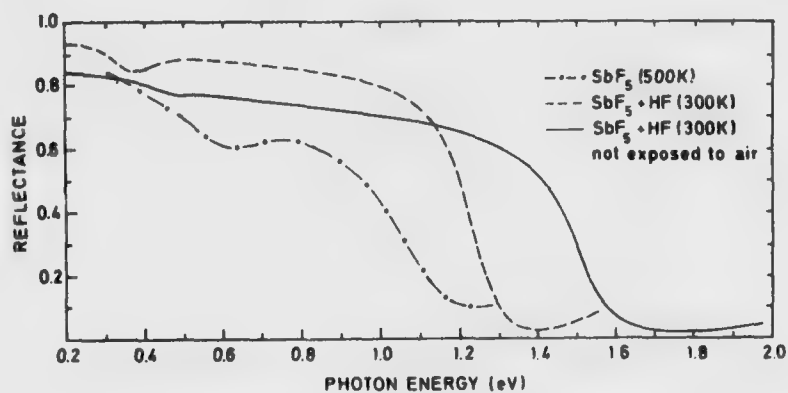
Figure 8 The first stage compound C_8K Figure 9 Reflectance of several SbF_5 graphite compounds

Table I

Material	$\sigma/\sigma(cu)$ a-axis 300K
graphite	1/30
C_8K - stage 1	1/6
HNO_3 - age 4	1/3
BF_3 - ?	5/6
$SbF_5 + HF$ - stage 1	(1.4)*

* predicted from ω_p

physical properties involves close interaction with the materials preparation studies. The nature of the chemical reactions by which the compounds are formed are also under study. Thus simple experimental and theoretical techniques are being employed to try to get an approximate global picture of this class of materials. At the same time detailed studies are being carried out on a few representative compounds.

The array of distinct compounds is huge; about 60 different species are known to form intercalation compounds, and most of these can be made in at least 5 stoichiometric concentrations (or "stages"). The scope and nature of the graphite intercalation compound problem makes it ideally suited to the MRL approach.

B. Amorphous Magnetic Alloys

Experimental work on amorphous alloys was begun at Penn by Robert Maddin, who published (1969) the first method for the production of continuous lengths of amorphous alloys. His interest was principally in mechanical properties and in the transformation from the amorphous to the crystalline state, and much of his work was done on non-ferromagnetic alloys such as PdSi. He and his students made some ferromagnetic alloys, and a few magnetic measurements were carried out. Intrinsic rather than structure-sensitive properties were examined--saturation magnetization vs. composition, etc.

Partly as a result of Maddin's work, the Materials Research Center of Allied Chemical Corporation began in the early 1970's to make amorphous alloys on a relatively large scale. Allied's interest at that time was in mechanical properties. Late in 1973, Allied announced publicly the availability of long lengths of amorphous ribbons for evaluation and testing by others.

The fact that the Allied ribbons were available in long lengths of uniform cross-section, plus Allied's clear interest in engineering applications, immediately suggested measurements of the low-field properties, using toroidally-wound ribbon samples. C. D. Graham, Jr. and Takeshi Egami initiated a study of the magnetic properties of these amorphous alloys in the LRSM in February 1974. As a result of the excellent magnetic measurements capability, it was quickly discovered that these alloys had extraordinarily low coercive fields and high permeability, i. e., they were good soft magnetic materials as shown in the figure.

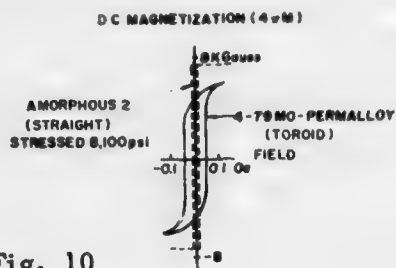


Fig. 10

An abrupt break in the magnetization curve at about half the saturation magnetization (behavior unexpected in a material which presumably has no anisotropy) caused an initial problem. However, measurements of the magnetostriction (change in length on magnetization) suggested that stress effects might be important, and indeed it was found that elastic tension removed the break in the magnetization curve, greatly increased permeability, and lowered the coercive field--all highly desirable results. A patent application based on this discovery was filed in the summer of 1974, along with two others on annealing in a magnetic field and on the effects of mechanical rolling on magnetic behavior.

We have developed procedures within the LRSM to make our own amorphous sample ribbon utilizing the prior experience of Robert Maddin and his students. The early observation that the amorphous ribbons become brittle when annealed at low temperatures (temperatures too low to cause crystallization) has led to a number of related measurements, and to the conclusion that internal stresses left in the ribbon by the manufacturing process are quickly relaxed by low-temperature annealing. This relaxation has consequences for the magnetic properties, and offers the possibility for control of magnetic properties by annealing treatments under stress and/or in applied fields. A more general conclusion is that the amorphous structure is not unique, but that a range of structures is possible, all of which are, to an ordinary x-ray determination, amorphous. This aspect of the amorphous metal problem is being attacked by the new technique of energy-dispersive x-ray diffraction, using equipment and expertise available in the LRSM x-ray diffraction and electron microscopy facilities.

At present, work is proceeding along three general lines:

1. Applications. A search for improved alloys and treatments with the specific aim of providing materials for use in power transformers. This requires undertaking certain measurements, notably power losses, on samples very much smaller than those normally used. We think that

calorimetric methods will be most appropriate. 2. Structural studies. The energy-dispersive diffraction equipment has been assembled, and results are just beginning to be collected. 3. Mechanical property measurements. Creep measurements are being undertaken both as matters of interest in their own right, and as means of interpreting the amorphous structure and its reaction to annealing and deformation.

We were able to move quite rapidly in this field, largely because of the facilities and expertise available at LRSM, and because of the flexibility in funding that allowed rapid response. As a result, the LRSM has become one of the two or three leading centers of research on amorphous magnetic alloys, and the only University center, in the United States.

IV. THE RESEARCH PROGRAM

In this section we present brief accounts of individual LRSM research projects, including projects supported through LRSM by NSF and projects supported by other agencies.

A. SURFACES AND INTERFACES

1. Kinetics of Surface-Catalyzed Reactions

W. R. Brennen, Associate Professor of Chemistry

Research Assistant: M. E. Shuman

Support: NSF/MRL

Objective and Approach: The objectives of this work are i) to develop new experimental techniques for investigating the kinetics and mechanism of elementary chemical processes which take place at phase boundaries, particularly at the gas-solid interface, and ii) to explore rational modification of surface molecular structure by physical and chemical means as a way of controlling catalytic activity.

Currently we are investigating the kinetics of recombination of gaseous nitrogen atoms on various interesting and important kinds of surfaces having a wide range of catalytic activity, such as amorphous silica in various forms and supported metallic films.

At present our approach is macroscopic and involves experimental measurement of the time dependence of atomic concentration in a gaseous sample with access to a catalytic surface combined with computer modeling which incorporates the details of various likely mechanisms of the molecular events at the surface.

This work is a fundamental aspect of the general problem of heterogeneous chemical catalysis, and it is hoped that the results may contribute to a better understanding of the kinetics of surface processes at the molecular level.

Progress: To observe surface-catalyzed recombination of nitrogen atoms under circumstances which may afford some information regarding the

initial non-steady-state phase of interaction between the atoms and a fresh surface, we have redesigned the classic (1943) Smith side-tube experiment in which a cylindrical tube, closed at one end, whose inner surface is the catalyst of interest and which contains inert background gas, is permitted to communicate with a reservoir containing a constant concentration of atoms dilutely dispersed in the same background gas. The atoms diffuse through the background gas into the side tube, interact with the walls and eventually set up a stationary distribution of atomic concentration within the side tube. The older work involved comparison of the form of the experimental stationary distribution with that predicted by an approximate analytical model. We are interested in how the atomic concentration at any point along the side tube is built up as a function of time to its stationary value. To model this kind of experiment requires solving the diffusion equation supplemented by a term to account for homogeneous recombination, the rate of which depends on the square of the atomic concentration in the gas, thus:

$$D \nabla^2 n - kn^2 = \frac{\partial n}{\partial t} \quad (1)$$

where n is the atomic concentration and depends on spatial coordinates and the time, D is the binary diffusion coefficient of atoms in the background gas, and k is the product of the intermolecular homogeneous recombination rate constant and the pressure. Whereas the diffusion and homogeneous recombination merely govern the rate at which atoms strike a given patch of surface at a given time, the kinetic attributes of the surface process, which is the thing of interest, must be incorporated into the boundary condition which expresses the net rate at which atoms appear to vanish upon hitting the surface either because they adsorb or because they react with a previously adsorbed atom to form a molecule. The overall probability that an atom will not survive an impact with the wall is called γ . Our previous theoretical work has made it amply clear that γ may in general be expected to depend on the time, $\gamma(t)$, and how the time dependence of γ is related to the details of the recombination mechanism at the surface. Previous surface recombination studies, having been conducted under stationary or quasi-stationary conditions, have treated γ as a constant quantity.

Using a recently-developed numerical procedure, we have written and tested a computer code to solve Eq. (1) for cylindrical geometry in a tube of finite length with time-dependent boundary conditions to accommodate $\gamma(t)$ arising from the Langmuir-Rideal two-step adsorption/abstraction mechanism, which we are using to analyze our experiments.

On the experimental side, we have constructed a side-tube apparatus fitted with a spring-actuated gate, which is permeable to

inert gas but not to nitrogen atoms, that can be moved aside in a few milliseconds to allow atoms to enter the side tube from the adjacent reservoir. The build-up of atomic concentration at any point along the tube may be followed photoelectrically and recorded by photographing an oscilloscope trace which is triggered by the mechanical gate.

Preliminary results are encouraging in that the form of observed atomic concentration time histories in a fused silica side tube cannot be simulated with a solution of Eq. (1) computed using any constant value of γ ; however, these results can be fitted accurately by means of solutions computed using a qualitatively reasonable form for $\gamma(t)$. It appears, therefore, that we have succeeded in gaining experimental access to the initial, non-steady-state phase of the surface process and that new information about the mechanism of the surface process may be obtained.

2. Optical and Acoustical Spectroscopy of Solids

E. Burstein, Professor of Physics

Postdoctoral Fellow: A. K. Hjortsberg

Research Assistants: S. P. B. Buchner
W. Chen
Y. -J. Chen
L. -Y. Ching
G. Ritchie

Support: NSF/MRL
ARPA
ONR
ARO-D
IBM

Objective and Approach:

A. To study the linear and non-linear properties of surface elastic and electromagnetic waves which propagate along surfaces or interfaces of dielectric, metallic and magnetic media in order to elucidate the basic properties of surface waves and to develop surface wave spectroscopic techniques for the investigation of surfaces and interfaces.

B. To study experimentally and theoretically the inelastic scattering of light by elementary excitations in order to elucidate the fundamental mechanism of light scattering in solids including the effects of finite wave vector and applied fields, and to develop light scattering as a probe of the electronic properties of solids and surfaces.

Our major short range goals are: i) to use the field-induced Raman scattering by LO phonons as an electromagnetic probe of the surface space charge regions of III-V compounds; ii) to explore the use of surface electromagnetic waves as the excitation source in non-linear optical phenomena, and (iii) to explore the use of surface electromagnetic waves as spectroscopic probes of chemisorbed atoms and molecules on metal surfaces.

Progress:

i) Our data on resonance-enhanced light scattering by LO phonons indicate marked differences in the character of forbidden LO phonon scattering at the (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces of n- and p-InAs, which reflect the

differences in the location and pinning of the Fermi level, relative to the band edges, at the two surfaces. These data together with the effects of an external electric field, applied by means of an electrolytic cell, indicate that the electric fields at the (111) and ($\bar{1}\bar{1}\bar{1}$) surfaces point in opposite directions and that the energy bands bend upwards at the surfaces of both n- and p-InAs. This work is continuing.

ii) Using surface electromagnetic (SEM) waves generated by prism coupling at a Ag-liquid benzene interface of a Kretschmann ATR configuration we obtained an enhancement in the Raman scattering by liquid benzene of ≈ 75 . This enhancement is a direct manifestation of the strong electric fields at metal-dielectric interfaces that occur when SEM waves are excited by prism coupling. We are extending our experimental studies to other non-linear optical phenomena and to two photon absorption.

iii) We have shown by means of a general theoretical formulation that, by using SEM waves in an ATR prism configuration, it should be possible to enhance the intensity of Raman scattering by a thin overlayer on a Ag surface by two orders of magnitude. Our theoretical formulation is directly applicable to the use of SEM waves in light scattering by optical and acoustical phonons in metals. It is also applicable, with minor variation to the SEM wave enhanced second harmonic generation at a Ag-air interface.

iv) We have calculated the dispersion curves of the SEM modes which occur at a "quantized" surface layer on silicon by treating the layer as a very thin anisotropic plasma slab and taking into account the coupling of the SEM modes with the inter-subband electronic excitations of the surface quantized levels. Our results show that it should be feasible to determine the frequencies of the inter-subband excitations of the quantized plasma layer by means of attenuated total reflection (ATR) measurements using the silicon as its own ATR prism. They also show that the resonance frequency of the inter-subband electronic transitions is shifted to higher frequency by the associated "longitudinal" electric field. A more realistic model which takes into account the spatial dependence of the wave function of the electrons in the surface space charge region is under investigation.

v) We are now exploring the effects of the sizeable propagation of SEM waves at metal-air interfaces on ATR measurements that occur when using incident volume EM beams in the infrared whose cross-sections are small compared to the propagation lengths but large compared to the wave lengths. Under such conditions, one observed a very large Gooch-Hansch, i. e., "beam displacement", effect, and one must develop new procedures for obtaining meaningful ATR data. Our results thus far

indicate that it should be possible, using the ATR prism configuration, to obtain meaningful data on both the dispersion curves and propagation lengths of the SEM waves.

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3. a. Hyperfine Interactions in Rare Earth Compounds
- b. Bonding and Interaction of Surface Atoms and Molecules on Single Crystal Surfaces

M. E. Caspari, Professor of Physics

Postdoctoral Fellow: D. J. Bellafiore

Support: ARPA
NSF

Objective and Approach:

A. The purpose of this aspect of the program is an experimental study of the magnitude and symmetry of hyperfine interactions and associated relaxation mechanisms in the rare earth garnets and rare earth monochalcogenides by γ - γ perturbed angular correlation and Mössbauer experiments.

B. Vital to the development of a microscopic model of chemisorption is a knowledge of the fundamental atomic processes involved in surface reactions and a knowledge of the location of the reaction sites of atoms on the surface. Information regarding the geometric location of single adatoms on a surface will be obtained from hyperfine interaction measurements using perturbed angular correlations and will be correlated with the results from field ion microscopy (W. Graham) and angular resolved photo-emission and Auger spectroscopy (Plummer and Gustafsson) experiments using the same surfaces and adatoms. Macroscopic phenomena such as clustering and island formation of adatoms which are influenced by imperfections, such as step edges, will be studied by detecting the changes in the symmetry of the wave functions as a function of coverage and substrate temperature. The results will be correlated with field ion microscopy studies of microscopic surface diffusion.

Progress:

- A. 1. Sn^{3+} Transferred Hyperfine Field in the Europium Monochalcogenides Doped with Tin Monochalcogenides

EuS , EuSe , and EuTe (but not EuO) are found to form solid solutions with the corresponding tin monochalcogenides. Transferred hyperfine fields (~ 50 kOe) observed at the tin nuclei in dilute solid solutions using Mössbauer spectroscopy are shown to be supertransferred from the 2nd Eu neighbors.

This work is now in its final phases.

2. PAC Study of Hyperfine Interactions in $^{154}\text{Gd}^{3+}$ in Rare Earth Garnets

The time-integral attenuation coefficients of the 1274/123-keV γ - γ cascade in ^{154}Gd were measured in the temperature region 4.2 - 650 K for $^{154}\text{Gd}^{3+}$ incorporated in GdAlG and GdIG substitutionally and in YAlG and YIG as an impurity. Rotation measurements were also made on the same cascade in the iron garnets at room temperature with an applied magnetic field in the range 0 - 15 Kgauss.

Employing independent measurements and calculated estimates of the static hyperfine magnetic field and EFG, the observed data could be interpreted in terms of reasonable values of the correlation times of the $\text{Gd}^{3+} 4f$ -electrons. The correlation times were found to range from about 0.13 nanoseconds in YIG to about 1.30 nanoseconds in YAlG with GdAlG having a value of approximately 0.71 nanoseconds. In the case of GdIG , a self-consistent analysis of the data required a value of the lattice EFG which was larger than that estimated from the nearest neighbor point ion model. The correlation time in GdIG was then found to be the same as in YIG .

This work has now been completed.

B. Surface Hyperfine Interaction Measurements

It is the object of this research to obtain information regarding the adsorption site and the binding of the adsorbed atoms on a single crystal surface from hyperfine interaction measurements on the adsorbed atom deposited on clean macroscopic single crystal surfaces, as a function of coverage and substrate temperature.

For non-magnetic adatoms and atoms on the surface of the substrate, the hyperfine interaction is determined by the interaction of the nuclear quadrupole moment with the electric field gradient (EFG) set up by the electrons in the immediate vicinity of the nucleus (quadrupole interaction). If the nuclear quadrupole moment is known, a measurement of the quadrupole hyperfine interaction on the adsorbed atom on a surface therefore provides information regarding the electronic wavefunctions surrounding the adatoms. For a determination of the quadrupole interaction of adsorbed atoms on surfaces the technique of integral and time dependent perturbed γ - γ angular correlations (PAC and TDPAC), is very suitable for the following reasons:

1. The number of atoms required for the experiment is small ($< 10^{10}$) relative to the number of sites on easily obtainable clean single crystal surfaces, so that experiments with low coverage are possible.

2. Since the experiment is performed with specific radioactive isotopes deposited on the surface, the properties being measured are those of surface rather than bulk atoms.

Presently we are studying the quadrupole interaction of adsorbed cadmium and hafnium atoms using the radioisotopes ^{111m}Cd and ^{181}Hf deposited on clean single crystal surfaces of tungsten and nickel in ultra-high vacuum as a function of coverage and substrate temperature. These results will be correlated with field ion microscopy studies by W. Graham and angular resolved photoemission and Auger spectroscopy experiments by W. Plummer and T. Gustafsson carried out on the identical adatoms and substrates. It is expected that the information obtained from this combination of experiments, together with theoretical calculations by J. R. Schrieffer and P. Soven will not only determine the location of the adsorption sites but also provide an estimate of the bond lengths and nature of bonding of the adatoms to the surface atoms. From experiments on the hyperfine interactions as a function of coverage and temperature one can obtain information on the temperature dependence of ordered overlayer growth and clustering and island formation. This is governed by diffusion processes on a macroscopic scale which should be influenced by surface faults such as steps, etc. Such faults can be artificially introduced on the surface and their influence on the processes of clustering can be studied and compared with the microscopic diffusion results and the temperature of the ordered overlayer growth as observed from field ion experiments.

Publications:

Bykovetz, N., " Sn^{2+} Transferred Hyperfine Fields in the Europium Monochalcogenides Doped with Tin Monochalcogenides", Solid State Commun. 18, 143 (1976)

Bellafiore, D. J., "PAC Attenuation Coefficients G_{22} and G_{44} for a Randomly Oriented Non-Axially Symmetric Static Electric Quadrupole Interaction for the Intermediate Spin $I = 2$ ", Hyperfine Interactions (Accepted)

4. Statistical-Mechanical Studies of Fluids and of Adsorbed Layers on Solid Surfaces

D. D. Fitts, Professor of Chemistry

Postdoctoral Fellow: W. G. Madden

Research Assistants: E. D. Glandt
W. J. Welsh, Jr.

Support: NSF/MRL
U of P

Objective and Approach: From a knowledge of the interactions among molecules, it is possible in principle to predict the structure and the macroscopic properties of materials and the dynamics of processes. Thus, the objective of our overall research program is two-fold: to evaluate the potentials of interactions for various systems as quantitatively as possible and to study by means of statistical mechanics the influence of these potentials on the structure and properties of macroscopic systems.

The technological importance of adsorption in the fields of lubrication and detergency, of catalysis, of oxidation and corrosion of surfaces, and of isotope separation has led us to explore the fundamental molecular processes involved. One aspect of our studies concerns the determination by statistical mechanics of the thermodynamic properties, including phase transitions, of molecular monolayers adsorbed on uniform and nonuniform solid surfaces. Recent work by others has dealt with dilute monolayers of atomic species. We are extending the theory to dense monolayers of spherical molecules and to dilute and dense monolayers of nonspherical molecules. Another aspect of this study concerns the intermolecular potential functions for adsorbate-surface interactions and the influence of surface sites on the adsorbate energy levels.

The application of statistical mechanics to determine structure and macroscopic properties from the known or assumed form of the intermolecular potential is often a difficult mathematical task. We are applying perturbation techniques to the distribution function procedures of the theory of fluids in order to calculate quantitatively the structure and thermodynamic properties of simple and polar fluids. Our goal is to develop a scheme for determining the structure and bulk properties for highly-structured liquids such as water.

Progress:

Statistical-mechanical treatment of monolayers

The adsorption of large spherical molecules such as Ar or Kr on effectively uniform surfaces such as graphite can be treated by the mobile-monolayer model, in which the adsorbed molecules are free to move in a plane parallel to the solid surface. Thus, the adsorbed layer behaves to a good approximation as a two-dimensional fluid. Accordingly, we are determining the radial distribution function, internal energy, and pressure for a large number of thermodynamic states of a two-dimensional fluid whose molecules interact via the widely-used Lennard-Jones pair potential. Three different approximate techniques, namely the Percus Yevick (PY) integral equation, the hypernetted-chain (HNC) integral equation, and a perturbation theory, have been used. We solved the PY and HNC equations by two distinct methods and obtained essentially identical solutions. These are the first HNC and only the second PY calculations on the two-dimensional Lennard-Jones fluid to be published. (Moreover, the first PY results, obtained by F. Mandel, are in error.) The perturbation theory calculation makes use of our PY and HNC solutions. When the results obtained from these three procedures are compared with computer simulations for the two-dimensional Lennard-Jones fluid, we find that the perturbation theory gives the best overall agreement with the radial distribution function. Our studies of the thermodynamic properties are well along, but are not yet completed. Some preliminary work has already been published in the Journal of Chemical Physics.

Perturbation theory of fluids

We have applied statistical-mechanical perturbation schemes to determine the radial distribution function for the three-dimensional dipolar and quadrupolar Lennard-Jones fluids. We selected the Lennard-Jones fluid as the reference or unperturbed system and calculated the first three terms in the perturbation expansion of the angle-averaged radial distribution function using an HNC approximation which we had developed earlier. While the second-order results agree qualitatively, but not quantitatively, with computer simulations, the addition of the third-order term gives much poorer results, indicating that the perturbation expansion converges too slowly for practical use. We did find, however, that the use of a Padé approximant involving only the terms to third-order gives excellent agreement with the computer simulations. These results have been accepted for publication in Molecular Physics. In collaboration with Dr. W. R. Smith at Dalhousie University (Halifax, Nova Scotia) we are applying this technique to the dipolar and quadrupolar hard sphere fluids. These discoveries will be carried over to the two-dimensional case in our upcoming work.

In collaboration with Dr. D. Henderson at the IBM Research Laboratory (San Jose, California) we have determined by means of the Monte Carlo computer simulation procedure and have calculated with the HNC theory the radial distribution function and the equation of state for the square-well fluid over a wide range of temperatures and densities. The square-well potential is very useful for testing theories of fluids. Not only is the square-well fluid a qualitatively reasonable approximation to real simple fluids, but also in perturbation theory calculations the complicating effects of a soft core are not present. Thus, studies with this potential form enable one to establish features common to all perturbation theories. Moreover, the square-well potential has the further characteristic that the second- and higher-order perturbation terms are relatively large so that one can assess easily the relative merits of various schemes of calculating these higher-order terms. The results of these determinations have been accepted for publication in the Journal of Chemical Physics.

Adsorbate-surface interactions

We have completed our analysis of the interaction between an adsorbed diatomic molecule and a solid surface using an anisotropic potential form proposed by Neilson and Gordon. As a test of the general procedure we used the parameters characteristic of the interaction between a single HCl molecule and an Ar atom. The potential energy of interaction between a single HCl molecule and the crystal surface was obtained for a variety of positions by directly summing the individual HCl-Ar interactions over the Ar lattice sites. The minimum potential energy occurs when the HCl molecule is at a tetrahedral-hole site on the (111) face of solid Ar and at temperatures below 30 K the HCl molecule can be considered as localized at that site. The quantum-mechanical rotational-vibrational energy levels of the adsorbed HCl molecule were calculated using a semiclassical technique to separate the Schrödinger equation.

Publications:

Smith, W. R., Madden, W. G. and Fitts, D. D., "Perturbation Theory and the Radial Distribution Function of Fluids with Nonspherical Potentials", Chem. Phys. Lett. 36, 195 (1975)

Glandt, E. D. and Fitts, D. D., "Solution of the PY and HNC Equations in Two Dimensions", J. Chem. Phys. 64, 1241 (1976)

Madden, W. G. and Fitts, D. D., "Integral-Equation Perturbation Theory for Polar Fluids", Mol. Phys. (Accepted)

Henderson, D., Madden, W. G. and Fitts, D. D., "Monte Carlo and Hyper-netted Chain Equation of State for the Square-well Fluid", J. Chem. Phys. (Accepted)

5. High Resolution Microscopy of Crystal Interfaces

W. R. Graham, Associate Professor of Metallurgy and Materials Science

Research Assistant: P. G. Flahive

Support: NSF/MRL
EPRI
NSF

Objective and Approach: The development of a microscopic model of surface interactions with predictive capabilities would be considerably aided by the availability of quantitative data on the interactions and geometric location of single atoms adsorbed on well defined single crystal surfaces. To this end the single atom resolution capabilities of the field ion microscope are being utilized for the following studies:

a) a determination of the crystallographic dependence of bonding on the nickel surface from a study of the diffusion of single atoms on several of the low index planes of the nickel surface

b) a determination of the geometric location of single adsorbed atoms on tungsten and nickel surfaces from high resolution field ion and field desorption observations.

Our studies involve nickel because of the interest in its catalytic properties and because it is amenable to theoretical modeling, and also tungsten, because of the wealth of experimental information available for tungsten surfaces.

Progress: The first of two highly specialized field ion microscopes designed for surface studies has been completed, undergone initial testing, and is now being used for the study of surface reactions.

Initial testing showed that vacuums of 10^{-10} torr are readily achievable with the normal ultra-high vacuum processing procedures and that the microscope meets the ultimate resolution capabilities and this type of unit, namely clear resolution of the adjacent atoms in the close packed (211) rows of tungsten, spacing 2.74 Å.

The two initial studies being undertaken with the microscope are the study of diffusion characteristics of nickel atoms on single crystal surfaces and the determination of the surface sites occupied by tungsten atoms during the diffusion process.

Preliminary studies of the diffusion of single nickel atoms on tungsten surfaces have shown that nickel atoms are very weakly bound to the tungsten surface but that useful information on the nature of interactions of nickel atoms with single crystal surfaces can be gained with the use of neon as an imaging gas. Work on tungsten surfaces will be continued and will provide a base for comparison with the results to be obtained for self diffusion on nickel surfaces.

The second experiment now underway is a determination of the surface sites occupied by a tungsten adatom during the diffusion process. This experiment was designed to answer the important question of whether a diffusing adatom can occupy sites other than lattice or equilibrium sites on a surface during the diffusion process. The accuracy of data obtained from diffusion experiments has now reached such a level that it has become imperative that an answer to this question be obtained. The extremely high resolution of the existing microscope allows a straightforward approach to this experiment and these measurements are at present progressing quite satisfactorily.

A second system is now under construction and on completion will be used for the preliminary work on direct determination of binding sites.

Publication:

Graham, W. R., Ehrlich, G. and Stolt, K., "Surface Diffusion of Single Atoms and Atom Clusters", Proc. 22nd Int. Field Emission Symposium, Atlanta, Georgia (1975)

6. Photoemission Studies with Synchrotron Radiation

T. Gustafsson, Assistant Professor of Physics

E. W. Plummer, Associate Professor of Physics

Research Assistant: C. Allyn

Support: NSF/MRL

Objective and Approach: Our aim is to try to understand the electronic properties of clean and adsorbate covered surfaces. This is a fundamental parameter for the understanding of chemical reactions. Although our own interests are of a basic nature, it is commonly believed that this field will have a large input on problems of a practical origin, e. g., catalysis and corrosion.

The experimental technique that we are using is photoelectron spectroscopy. What sets us apart from most groups using this technique is the heavy emphasis on synchrotron radiation. This powerful light source has several unique characteristics. It is intense, polarized and most important, continuous.

During the last year, we have worked towards an understanding of the electronic structure of the clean metal on the one hand, and of the free molecule on the other. We have also built an electron spectrometer that will allow us to obtain unique information about the interaction of these components.

Progress: We have completed our measurements of the clean W surface. These results show clearly the importance of band structure effects in photoemission. The detailed theoretical interpretation of these data is in progress.

We have in progress a large scale investigation of the partial photoionization cross sections of simple molecules. Using synchrotron radiation, we have for the first time obtained such data as a continuous function of wavelengths. Our data for CO and N₂ have been coupled with a theoretical calculation by J. W. Davenport. They show the fundamental importance of an understanding of the final state in the photoionization process. Together, they form the first quantitative experimental and theoretical understanding of cross sections in photoemission from molecules. Recent data from CO₂ and SF₆ show further examples of such final state resonances (in the case of SF₆) only some ten times more pronounced!! Our measurements on Xe show the need to go beyond a single particle interpretation for an interpretation of our results and will provide needed data for a discussion of the validity of the RPAE (= Random

Phase Approximation with Exchange). The data on O_2 and NO show dramatic deviations from a straightforward Franck-Condon picture. Other investigated molecules include N_2O , H_2CO , H_2O , and CH_4 .

The major effort over the last 6 months has gone into the construction of a unique electron spectrometer. With it, it will be possible to measure the energy distribution of photoemitted electrons as a function of emission angle of the electron and incidence angle of the photon. The unique property is that virtually all combinations of these angles will be obtainable independently. The spectrometer is now being tested and is now being tested and is expected to be used routinely by the end of the summer.

7. Reaction Kinetics and Mechanisms

J. G. Miller, Professor of Chemistry

Research Assistants: J. J. Davis
G. A. Parodi
B. Vessal

Support: NSF/MRL

Objective and Approach: The objective of our research is to determine how some chain reactions are started. We are studying two chain reactions, one that is initiated at a metal surface and one that is initiated by light radiation.

The reaction initiated at a metal surface is the reaction of halogenated hydrocarbons with amines, which are hydrocarbon derivatives of ammonia. The course of the reaction after it has started is now well known, but the initiating processes are quite varied, complicated, and incompletely understood.

There are four different initiators known for this reaction to date: light radiation, a copper-metal surface, iron and copper ions, and a glass surface containing aluminum oxide. The details of the photochemical initiation have been worked out here, but the details of the other three triggering processes need more study.

The initiation at the copper-metal surface is our chief present interest. It has broad general interest because of its relation to the mechanism of corrosion of metals, because of its use in the application of the haloalkane-amine reaction to the formation of commercially important polymers, and because of the information it can yield for the understanding of many other reactions at liquid-solid interfaces.

The other chain reaction studied by our group is the one occurring in the photolysis of peroxides. Here we are working with both the initiating and propagating steps in the photolysis of peresters.

Our approach uses a combination of chemical and physical methods. It is fundamentally a study of the kinetics of the initiation under a variety of chemical conditions coupled with physical observation of the changes in the structures of the surface and of the reactants attached to that surface.

Progress:

1) The haloalkane-amine reaction.

The initiation of the reaction at a copper metal surface was discovered by our group and we have established the principal chemical features of the process: the preliminary attachment of oxygen to the surface followed by attachment of amine, and finally reaction of the haloalkanes with the attached amine. We are now studying the way in which the amine is attached to the metal surface so that it is rendered reactive toward the haloalkane.

During this year we have started study of the mode of attachment of the amine molecules by measurement of their in situ absorption of infrared light, using the method of attenuated total reflection. Although the technique is a difficult one, the improvement we have obtained in the spectra has encouraged us to continue these measurements. The speed of reaction with thin films of copper metal complicates the study.

We have also continued study of the use of sulfur in place of oxygen as activator of the copper surface. These studies have shown that sulfur does perform the same function as the oxygen and will allow more definitive study of the process. The techniques of purification and handling of the reagents and for exclusion of oxygen that we have been forced to develop will be of general utility for study of the reaction for other purposes also.

The related process of initiation by copper ions has been investigated. Cu^{2+} ions complexed with different ligands were used. The results showed that the stronger the attachment of the ligands to the Cu^{2+} ions, the lower the rate. Since the strength of attachment is probably proportional to the electron donor capacity of the ligand, it appears that in its initiating action the Cu^{2+} removes an electron from one of the reactants. A study of initiation by Co^{2+} , Ni^{2+} , and Zn^{2+} ions is also underway.

2) The photolysis of peresters.

The photolysis of t-butyl perlaurate in the neat condition has been found by us to depend remarkably strongly upon the purity of the perester. The photolysis is inhibited by small amounts of the pyridine which is used in the synthesis of the perester. We have developed a reliable method of removing the pyridine completely and have found that the quantum yield is more than trebled by the removal.

We have found that photolysis of the pure perester follows $3/2$ -order kinetics with a quantum yield of decomposition of approximately 7, indicating a free-radical chain mechanism. EPR spectroscopy showed that the free radical is an alkyl peroxy radical. A small amount of pyridine enhanced the signal strongly. Apparently a charge-transfer complex is formed between the alkyl peroxy radical and the pyridine. We have found that little or no aliphatic carboxylic acid is produced in the photolysis of very pure perester.

8. Statistical Mechanics of Adsorption in Micropores

A. L. Myers, Professor of Chemical and Biochemical Engineering

Research Assistants: E. D. Glandt
C. Minka
J. Soto

Support: NSF/MRL
Mobil
ERDA

Objective and Approach: Adsorption on flat surfaces has been studied exhaustively but there are no practical equations for adsorption in microporous adsorbents. This is surprising in view of the industrial importance of zeolites for separations and catalysis.

Adsorption in micropores is given theoretically by the equation:

$$\bar{N} = \frac{\sum_i Z_i (P/kT)^i / i!}{1 + \sum_i Z_i (P/kT)^i / i!}$$

where the summation terminates at M, the capacity of a cavity (10-20 molecules). Z_N is the configuration integral for N molecules in a cavity and even Z_1 is a complex summation over hundreds of atoms in the lattice followed by integration over the cavity. So far, attempts to calculate configuration integrals from first principles have been unsuccessful because of the lack of a quantitative theory of intermolecular forces. Therefore our approach is to use experimental data for the first configuration integral (Z_1) as a probe of adsorbate-surface intermolecular forces. Given intermolecular potentials for adsorbate interactions with lattice atoms, one can calculate the higher configuration integrals and thus generate all of the equilibrium properties of adsorption at different temperatures from low pressure up to saturation.

Monatomic gases (Ar, Kr, Xe) are ideal molecular probes because complexities of polarity and hindered rotation are removed. Also, need for removal of krypton and xenon formed during fission of nuclear fuels provides a practical motivation for these studies.

Progress:

Adsorption of Nonpolar Molecules in Zeolites at Low Pressure

We have developed a theory of adsorption in zeolites. A Lennard-Jones-Devonshire model for the interaction of a gas molecule with the

cavity atoms contains a single constant for the depth of the energy well. All other constants are obtained from crystallographic data. We use experimental data for the first configuration integral (one molecule in a cavity) as a probe for adsorbate-surface intermolecular forces. Given this constant, one can calculate the higher configuration integrals using known intermolecular potentials for the gas molecules and thus generate all of the equilibrium properties of adsorption at different temperatures from low pressure up to saturation (10-15 molecules per cavity).

Our objective is to reduce published experimental data for adsorption of various gases (Ar, Kr, Xe, CH_4 , O_2 , CF_4 , etc.) on zeolites (4A, 5A, 13X) to values of intermolecular energy parameters for each gas. The theory can be applied to predict adsorption equilibria of gases and their mixtures.

New Process for Separation of Gases

Adsorption is used primarily for purification of gases and liquids, but not for separation of 50-50 gas and liquid mixtures. We are developing a new apparatus for separating gas mixtures such as air into its constituents by adsorption. This is a joint project with Prof. F. Moser, Technische Universität, Graz, Austria, which began last year as an outgrowth of our LRSM work on adsorption from liquid mixtures. The process achieves the countercurrent flow required for staging by slurring zeolites powders in an inert liquid whose molecules are too large to penetrate the zeolite cavities.

Monte Carlo Calculations of Adsorption in Molecular Sieves

This is our most important theoretical result from LRSM work. We have shown by Monte Carlo calculations of radial distribution functions of 1-10 gas molecules in zeolite cavities that cooperative forces between these gas molecules are reduced by partial localization on sites of high energy. Recently published results by Ruthven (July, 1976) suggest that a hard-sphere model for gas-gas interactions is adequate. We find, on the contrary, that a hard-sphere model for gas-gas molecular interactions can be forced to fit the experimental data, but only by using unrealistic potential energy functions for gas-solid interactions.

Activity Coefficients of Adsorbed Mixtures

Recent experiments at the Universität Karlsruhe, Germany, show that adsorption of dilute solutes (phenol, p-nitrophenol) from aqueous solution on carbon are highly nonideal, in that the adsorption of phenol is drastically reduced by the presence of small quantities of nitrophenol,

whereas the adsorption of nitrophenol is hardly affected even by large concentration of phenol. Since waste waters always contain several components, these results have important implications for the removal of persistent organic pollutants from waste water. We have developed a theory that explains these and other data for adsorption from dilute liquid solutions.

Statistical-mechanical Treatment of Monolayers

The adsorption of large spherical molecules such as Ar or Kr on effectively uniform surfaces such as graphite can be treated by the mobile-monolayer model, in which the adsorbed molecules are free to move in a plane parallel to the solid surface. The work (with E. Glandt, D. Fitts) deals with a statistical-mechanical treatment of physical adsorption, the practical computation of adsorption isotherms, and the analysis of the corresponding experimental data. Theoretical calculations are in accurate agreement with published experimental data of adsorption isotherms both of Ar and Kr on graphite using only one energy parameter and the law of corresponding states for the gases. There is no other published theory with only one parameter which is in such good agreement with experimental adsorption and calorimetric data.

Publications:

Myers, A. L., "Adsorption of Nonpolar Molecules in Molecular Sieves at Low Pressure", A.I.Ch.E. Journal (Accepted)

Myers, A. L., "Equilibrium Adsorption of Gases by Suspensions of Solid Adsorbents in Liquids", Chem. Eng. Science (Accepted)

9. Electron Spectroscopy of Surfaces

E. W. Plummer, Associate Professor of Physics

T. Gustafsson, Assistant Professor of Physics

Research Assistants: C. L. Allyn
C. D. Ehrlich
S. P. Weeks
S. L. Weng

Support: NSF/MRL
NSF
Xerox
ARPA/LRSM

Objective and Approach: The objective of this program has not changed this year; it is to determine the fundamental properties of the chemical bond at a surface. The premise of this program is that such a fundamental understanding of chemisorption would surely accelerate the development of a mechanistic understanding of such practical materials oriented problems as Heterogeneous Catalysis, Corrosion, Embrittlement, Photocells and many Solid-State Electronic Devices. The achievement of such an objective necessitates a close coupling between theory and experiment, focusing, at first on a few carefully chosen systems. We will concentrate on the adsorption and interaction of simple diatomic molecules such as H_2 , CO , O_2 , and N_2 on well-defined metal substrates of the late transition elements, such as Ni, Fe, Co, Pd, etc.

The general approach is still unchanged: to use and develop modern electron emission spectroscopies to determine the bonding configuration of adsorbed molecules (both electronic and geometric), as well as the electronic and geometric properties of the clean metal surface prior to adsorption. Hopefully this experimental information can be coupled with theoretical models to answer the How's and Why's of our objective. The specifics of our experimental program have gradually changed due to the realization that in order to understand the photoelectron emission from adsorbed molecules we needed a more detailed knowledge of photoemission from gas phase molecules.

Progress:

1. Gas Phase Photoelectron Spectroscopy: (T. Gustafsson).

When a foreign molecule is adsorbed on a metal surface the photoelectron spectra from that molecule differs from the gas phase spectra for at least three reasons: (1) some electronic orbitals are involved in bonding;

(2) the measured binding energy of each electronic level is reduced due to the relaxation of the metallic electrons around the ion; and (3) the surface orientates the molecule causing strong angular dependent emission which is not present in the randomly oriented gas molecule. Obviously we would like to use the angular dependence mentioned in item 3 to measure the orientation of a molecule on a surface. The problem is that the angular dependence can not be measured. In the gas phase the molecule has random orientation and on the surface we don't know its orientation. In addition, the relaxation effects mentioned in item (2) above make the job of identifying the energy levels of a chemisorbed molecule from the measured binding energies very difficult.

During the last year Gustafsson and I have measured the absolute photoionization cross section of each of the valence levels of some 10 simple molecules as a function of photon energy, from threshold to 40 eV. The objective was twofold: (1) the frequency dependence of the cross section for a specific orbital is more of a fingerprint of that orbital than is the binding energy, so it can be used quite successfully to identify the levels of a chemisorbed molecule; and (2) to furnish detailed data for the theoretical calculation of J. W. Davenport and J. R. Schrieffer for partial photoionization cross section and angular dependent emission.

We have produced partial photoionization cross section measurements which were not available and most importantly a quantitative agreement was achieved for N_2 and CO with Davenport's calculations. We now know the angular dependent emission as a function of photon energy for the outer three levels of N_2 and CO.

2. Angular Resolved Photoemission: The understanding of the gas phase photoionization process is being used to determine the bonding configuration of molecules on the surface. The first experiments are on CO and N_2 , where the angle of detection is fixed and the crystal rotated with respect to the incident light to change the components of the electromagnetic field parallel and perpendicular to the surface. The CO data is consistent with a standing up molecule.

3. Angular Resolved Auger Emission: (S. P. Weeks). We have measured the angular dependence of the Auger emission from a single crystal Ni sample. The angular structure is quite pronounced and it has been suggested that the origin of this angular dependence is the scattering of the excited electrons from the periodic Ni structure. If this were true then the angular dependent emission from an adsorbed atom or molecule could be used to determine the geometry. A. Liebsch and Weeks calculated the angular dependence expected from point sources emitted and compared it to Weeks' data. Unfortunately they showed that the matrix

element for the Auger process is very important but unknown. Therefore I think we can lay to rest all of the expectations for angular resolved Auger emission.

4. Field Emission: (S. L. Weng). Due to a very close coupling with P. Soven and N. Kar, we have a much deeper understanding of the metallic surface resonance on tungsten. The measurements and calculations are now being done for Mo and Cu, which indicate a surface resonance on (100)Mo (like W) and a surface state on (111)Cu. The data on (100)Mo has shown that in agreement with the calculation of Kar and Soven on W(100), the surface resonance has large components of momentum parallel to the surface.

Publications:

Vorburger, T., Penn, D. and Plummer, E. W., "Field Emission Work Functions", Sur. Sci. 48, 417 (1975)

Soven, P., Plummer, E. W. and Kar, N., "Field Emission Energy Distributions", Critical Reviews in Solid State Science 6, 111 (1976)

Plummer, E. W., "Photoelectron Spectra of H_2 , CO, N_2 and C on (100) and (110)W", Progress in Surface Science (Accepted)

10. Theory of Chemisorption and Catalysis

J. R. Schrieffer, Mary Amanda Wood Professor of Physics

Postdoctoral Fellows: J. B. Danese
A. Liebsch

Research Assistants: J. W. Davenport
G. Loubriel

Support: NSF/MRL
ARPA/LRSM
NSF
American Gas Association

Objective and Approach: The scientific objective of this program is to develop a microscopic quantummechanical understanding of chemisorption bonds between atoms or small molecules and metal surfaces. Our interest is not only in the electronic structure of this bonding but also in the potential energy surfaces for surface chemical reactions and catalysis. Until recently, little quantitative work had been done on chemisorption binding in realistic situations. We have been employing the multiple scattering self-consistent field methods to determine both the electronic excitation spectrum and the total energy of the system as a function of the nuclear coordinants for simple complexes. This work has been done in preparation for applying such methods to extended surfaces and/or larger adsorbates. The results of this work are directed toward understanding both the geometry of the adsorbate and substrate in the chemisorption bond as well as the nature of the bonding orbitals in these systems. Potentially this work will have large impact on the fields of heterogeneous and homogeneous catalysis. Also there is hope that this work will ultimately have impact in the area of stress corrosion cracking.

Progress: Photoemission spectroscopy is perhaps the single most useful tool for the experimental study of surface phenomena. Analysis of the data, however, is not straightforward, essentially because the particle that is detected - the outgoing electron - is strongly coupled to the residual solid or molecule. These so-called final state effects appear even on the level of atomic and molecular spectroscopy and in a much more complicated form when photoemission spectroscopy is considered from extended systems. Consequently, we have invested a considerable amount of effort in developing methods and tools useful for the analysis of photoemission from a variety of classes of systems. J. W. Davenport has developed practical and efficient computer programs for calculating

the photoemission cross sections from oriented molecules. His techniques which go beyond previous work in that they are applicable to any type of initial molecular state, have been applied to several small molecules. The problem involves attempting a good representation of the initial state and equally good representation of the final, scattering-type state, and the optical matrix element connecting the two. He employed a multiple scattering technique based on a model of the molecule in which one has non-overlapping atomic potentials (the so-called muffin-tin approximation). One should note in this regard that while the molecular model greatly simplifies the complicated one-electron potential present in such highly anisotropic systems, the calculations are exact for the model potential proposed. Comparison with experiment indicates conclusively that approximate calculations for superficially more refined models are vastly inferior to Davenport's work. The technique has been applied to photoemission from high lying valence levels of carbon monoxide and nitrogen. Comparisons with the gas phase cross sections is in some cases excellent and invariably exhibits the correct functional form and energy dependence including resonances in the final state. In addition, Davenport compared his prediction for the angular resolved cross section from oriented but molecular CO to the extensive data of Plummer, Gustafsson, et al. on the chemisorbed species. The comparison proved extremely interesting. The presumed straight-up configuration of the molecule was confirmed. The angular and polarization dependence predicted by the theory was in excellent agreement with experiment.

The situations in which one can employ strictly molecular calculations to the study of chemisorbed species are relatively few. Extrapolation from the low energy electron diffraction situation suggest that just as the incident electron is multiply scattered by the crystal before being reflected, so the photoemitted electron will interact strongly with the adsorbing substrate. In order to treat such situations, A. Liebsch has carried out a series of calculations of the photoemission cross section from clean and adsorbate covered semi-infinite surfaces. His formalism is a multiple scattering one which incorporates the exact final state aspects present in the molecular studies but also includes the intrinsically solid state effects as well. In particular, the inelastic processes that ultimately provide the surface sensitivity that makes the spectroscopy such a useful one are incorporated in the theory by a phenomenological modification of the electron propagators. The first calculation carried out by Liebsch was for an "S-wave" photoemitter adsorbed on a model surface. The situation was analogous to photoemission from a core level. The calculation verified the importance of including multiple scattering in a theoretical analysis. Liebsch carried out detailed calculations for a realistic model of the layer compound TaS_2 , for which some experimental information exists in

the literature. The calculations were based on realistic initial states (for the Ta d-band) as well as multiple scattering and inelastically damped final states. Comparison with experiment was quite satisfactory. The overall shape of the experimental curves was reproduced and in many cases the relative heights and peaks of the valleys as well. Previous interpretations based on semi-classical ideas of shadowing of outgoing beams has proven incapable of explaining the data.

We have also worked on the problem of the bonding energy as a function of nuclear coordination using local density functional methods for handling exchange and correlation of effects. J. B. Danese has used the self-consistent multiple scattering scheme of Slater and Johnson to obtain molecular orbital wave functions which are then used to calculate the expectation value of the full local density functional Hamiltonian. This type of analysis leads to great improvement over the standard muffin-tin potential scheme. He investigated the binding curves for H_2 , C_2 , CO and N_2 to ascertain the intrinsic accuracy of the local density approximations. The results for H_2 are in quite good agreement with accurate numerical solutions on the local density functional equations by Gunnarsson and Johansson, suggesting that Danese's procedure gives a good approximation to the solution of these equations. However, the results for other diatomics treated are considerably poorer, giving a binding energy at the equilibrium spacing which is roughly half of the observed binding. It would appear that the difficulty arises largely from the breakdown of the local density approximation due to the rapid spatial variation of the density in the systems.

We have been attempting to improve the local density functional methods to include non-local effects, starting from first principles. Dr. Herbert Capellmann of the University of Aachen, Germany, worked on this problem during the year. Good progress was made and a paper is currently being written up with the results of this theoretical analysis.

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11. Electronic Structure of Surfaces

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Research Assistant: N. Kar

Support: NSF/MRL
NSF

Objective and Approach: The study of the properties of solid surfaces is an area of considerable activity at the present time. The two most commonly used experimental techniques are field emission, in which one observes the spectra of electrons emitted from the surface upon the application of a large electric field, and photoemission, in which one observes the energy and direction of electrons emitted from the surface upon application of an external optical field.

In contrast to experimental techniques used to investigate the interior of a solid, the surface specific techniques mentioned above require extensive theoretical analysis for their interpretation. Basically one must construct a model for the surface, and via a complicated non-linear type of analysis compare the predictions of the model with experiment.

Specifically, in this research project we are attempting to predict the observed field- and photo-emission spectra for a variety of materials, including tungsten, copper, and similar transition metals.

Progress: A prediction of the observed field- and photo-emission spectra from any material requires a detailed knowledge of the one-electron states of the solid. This follows from the fact that, apart from true surface-localized states, the one electron spectrum is determined by the bulk of the solid and it is only the surface induced modification of the wave functions that is being probed by the experiments. Accordingly, we have devoted a considerable amount of effort to the development of techniques for the calculation of one electron wave functions near the surface of a solid. We have fully developed and implemented (in the sense of computer programs) a scheme which allows the straightforward rapid, and accurate calculation of the one electron wave functions. One might add that extensive analysis of the structure of a one electron Hamiltonian in a semi-infinite solid was required for this development.

We have applied our methods to a prediction of the field-emission spectrum from tungsten, using a model of tungsten which was somewhat unrealistic in that it omitted the relativistic effects important in such a

heavy material. Such an analysis had been carried out already by other investigators using, I believe, somewhat inferior techniques. The results confirm in a general way those obtained by the previous investigators and indicate the extreme sensitivity of the observed spectra on the model employed.

We have applied our methods to a prediction of the spectrum for copper as well. The data is very crude - more is being taken at the present time - but comparison with the crude data suggest the essential correctness of our calculation.

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12. Electronic, Magnetic and Catalytic Effects Associated with the Interaction of Donor and Acceptor Molecules with Metallo Species

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Support: NSF/MRL
NIH
ARPA/LRSM

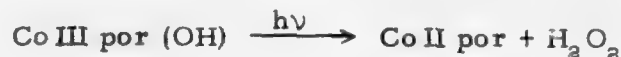
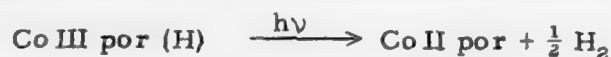
Objective and Approach: This study is focused on determining the influential factors for the binding of small molecules (O_2 , NO, CO, N_2 , SO_2) by metallo species and the mechanisms operative in modifying the electronic, magnetic and chemical reactivity properties through charge transfer interactions. Chemisorption, physisorption and the associated catalytic behavior of materials frequently result from donor-acceptor reactions. Interactions of this type may also be implicated in the introduction or modification of electrical conductivity and magnetic properties in materials. Interaction of small molecules with active binding sites of metallo species such as planar metal chelates, layered M-M bonded complexes and metals are studied, using spectroscopic and thermochemical methods. Variation of the metallo species and absorbate molecules provides a systematic chemical approach for identifying essential features for the interaction. Modified chemical behavior and catalytic reactivity of chemisorbed species is examined and correlated with models for the coordination effects on structure and electron distribution.

Progress: Metallo chelate complexes of Fe(III), Fe(II), Co(III), Co(II), Mn(II), Mn(III), Cr(III) and Cr(II) are found to reversibly add small molecules such as O_2 , CO, NO, N_2O and SO_2 . Molecular O_2 and NO bind cobalt(II) sites, forming adducts which can be described as containing coordinated O_2^- and NO^+ accompanied by effective oxidation or reduction of the metal ion. Contrasting chemical reactivities of metal-bound NO^+ and NO^- with O_2 and H_2O have been recognized. Evidence is available for the reaction of coordinated NO with a second NO to produce coordinated N_2O_2 , which is an important precursor in reducing nitrogen oxides. New nitric oxide complexes of Fe(III), Mn(II), Mn(III) and Cr(II) chelates have been prepared and shown to contain the NO^+ moiety. Co(II) species have been found which simultaneously bind O_2

and a donor molecule (CO), PX_3 , NX_3 . Catalytic oxidations have been observed for several Co(II) and Fe(II) systems. A general model for the interaction of diatomic molecules with metal sites has been developed and successfully applied to both structural and electronic features for complexes of O_2 , NO and CO. Iron II and Cobalt (II) macrocycles have been found to catalyze the oxidation of thiols (RSH) to disulfides (R_2S_2), which is important in desulfuration of petroleum.

Thermodynamic studies of the interaction of diatomic molecules with metal chelates has begun with the investigation of adsorption of CO by Fe^{II} porphyrin. Sequential addition of CO is found with production of $FeTPPCO$ and $FeTPP(CO)_2$. Equipment is currently being constructed for gas absorption by solids which will find application in surface-deposited metallo species.

Another new direction for this program is in photocatalysis. We have found that five-coordinate cobalt (III) macrocycles are photo-sensitive. A principal photo reaction is electron transfer from the anion to the cobalt center, resulting in reduction of the metal. This system has potential in the photocatalytic dissociation of H_2O into H_2 and O_2 .



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B. MATERIALS FAILURE CRITERIA

1. Craze Deformation of Polymers

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Research Assistant: B. Metzger

Support: NSF/MRL
ARO
U of P

Objective and Approach: Crazing is one of the two mechanisms whereby polymers deform and ultimately fail in service. The goal of the research is to qualitatively determine the fundamental parameters which characterize crazing and to observe how these parameters are effected by stress, strain rate, temperature, the environment, and the morphology of the polymer. It is expected that the fundamental interaction between these variables and the fundamental parameters which characterize crazing can be established. Hopefully crazing can be reduced to a few basic phenomena which can be quantified, so that new situations are analyzable with a minimum of experimental input. The short term goal is to determine the effect of environmental gases.

Progress: The macroscopic aspects of crazing have been derived from the basic equation

$$\dot{\epsilon}_c = \rho \gamma b \, da/dt$$

where ρ is the craze density or number of crazes per unit area of surface; γ is the surfaces to volume ratio of the specimen; b is the craze displacement or thickness and da/dt is the change in area of the craze with time. From the above equation, the following mechanical properties have been calculated: (1) the constant strain rate stress-strain curve; (2) the creep curve; and (3) the stress relaxation behavior. The above equation would enable one to predict the strain-time program that would be produced by a monotonic increase in stress with time or to predict the stress-time program if strain were increased monotonically. The next step is to predict the crazing behavior under an oscillating stress or strain.

Another accomplishment was to show how the pressure and temperature of various environmental gases affected craze deformation.

It was found that the tensile strength as determined by craze deformation could be described by the following equation

$$\sigma_c / \sigma_i = \left[\frac{p e^{Q/RT}}{p^*} \right]^{-n}$$

where σ_c is the tensile strength and σ_i is the tensile strength at the temperature T in an inert environment; p is the pressure of the environmental gas and P^* , Q and n are constants. For a given polymer n was independent of the gas (N_2 , Ar, O_2 , or CO_2). Q increased with the boiling point of the gas and was approximately equal to the heat of vaporization. For the three polymers, polycarbonate, polymethyl methacrylate, and polychlorotrifluoroethylene n had the values 0.13, 0.08 and 0.10. Now it is possible to determine the tensile strength of a new polymer in various gaseous environments over a range of temperature and pressure using the above equation and relatively few experiments.

By means of creep tests, the basic parameters which characterize crazing, ρ , b , and da/dt are being measured as a function of temperature, pressure of the gaseous environment, and stress. It was found that the craze velocity was the parameter which was most sensitive to changes in temperature and pressure. Previous experiments showed that ρ , the craze density, increases rapidly with stress and current experiments showed ρ increases moderately with P . The creep experiments indicate that P and T can be combined by using the effective pressure as the basic variable where the effective pressure is the pressure divided by the vapor pressure that would be in equilibrium with the liquid at a particular temperature. The relationship between ρ , b , and craze velocity and the number of layers of adsorbed gas is being established. It appears that the greatest effect is produced by the first two layers.

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2. Structure and Cyclic Response of Complex Materials

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Research Assistants: S. P. Bhat
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Support: NSF/MRL
NSF
ONR
ARO-D

Objective and Approach: Premature failure of machines by fatigue has been a problem for over 100 years and even now over 90% of fracture-type failures are caused by fatigue. Although design approaches have improved greatly since World War II, incomplete understanding of the mechanisms of fatigue is one reason why extensive testing is still required to validate the design of a new structure. The aim of the work here is to provide a better understanding of these mechanisms. A complete understanding of fatigue in relation to the many variables which affect its mechanisms is beyond the resources of a single institution. Consequently, the following aspects have been selected for study: 1) hardening caused by cyclic stressing (and softening, which occurs in some materials), 2) crack nucleation processes, and 3) the relation between cyclic deformation and the kinetics of fatigue crack propagation. The approach is to employ mechanical testing of carefully controlled materials in conjunction with electron microscopy.

Progress:

a) Cyclic Response of Complex Metals and Alloys

We have nearly completed a large study of the cyclic stress-strain behavior of the following aluminum alloys: both commercial and experimental-commercial alloys with different arrangements of second phases, ternary Al-Zn-Mg which is the basis of the commercial variants, and pure binary Al-Cu and Al-Ag alloys. In contrast to the Al-Cu alloy previously reported by us, none of these alloys undergo work-softening at high strain amplitudes. The Al-Zn-Mg alloy does show softening at

intermediate amplitudes (life in the range 10^4 to 10^5). These observations generally support the interpretation offered for the Al-Cu results, namely, "scrambling" of the smallest precipitates mainly responsible for the hardening. In the more complex alloys, the other microconstituents serve to homogenize the deformation and thus to prevent the localization of strain required to scramble the particles being cut by the dislocations. In addition, we have explored stress-strain response under variable amplitude loading for all the alloys; interesting comparisons have been observed with respect to constant strain amplitude tests and we now have a reasonable understanding of cyclic stress-strain behavior for different modes of loading. This work is continuing with emphasis on behavior at low strains.

The recent observation by Mughrabi that there exists a threshold, under plastic strain cycling, of 8×10^{-5} , below which persistent slip bands (PSB's) do not form has permitted us to extend our studies of copper single crystals. Since PSB's are known to be the sites of crack nucleation in most useful metals and alloys, their absence will cause 1) the matrix dislocation structure to carry the strain in a reversible manner and 2) the existence of a fatigue limit. On this basis, a fatigue limit (similar to that well-accepted for steels) has been claimed for most useful metals and alloys and its structure sensitivity explored. This result will be useful to designers.

b) High Strain Crack Nucleation

The mechanism of high strain crack nucleation has been explored in both wavy and planar slip metals. Two-beam interferometric studies have shown the surface morphological changes which occur under the action of large cyclic strains. The most important phenomenon for crack nucleation has been identified as the formation of a step at specific grain boundaries. The step, which ultimately grows about 5 microns high, forms at high angle grain boundaries with the primary slip system in one or both adjoining grains directed towards the intersection of the grain boundary with the surface, over a slip distance equal to the grain diameter. Replica's of the step profile have been used to show how the crack forms at the notch of the step with continued cycling. Previous theories of crack nucleation at high strains are inconsistent with these observations on the roles of grain boundary nature and slip geometry. This work is continuing.

c) Structures of Light Emitting Diodes

The misfit-compensating dislocation structures in a variety of heterojunctions have been explored by x-ray topographic methods (XRT)

on devices with very thin epilayers (to observe the initial formation of mismatch dislocations) and by stress-induced-birefringence techniques (SIB) and transmission electron microscopy (TEM) on devices with thicker, and final, epilayers (to find out how the dislocations subsequently arrange themselves). We have thus obtained a rather complete picture of the macroscopic and microscopic dislocation arrangements which permits us to discriminate the various mechanisms proposed for the formation of the dislocations. We have concluded that, for devices with mismatches in the range of 0.2%, and for crystals with [001] orientations prepared by vapor phase epitaxy, the great majority of the misfit dislocations are nucleated at the surfaces of the devices, probably at steps, glide into the interface as 60° dislocations and compensate misfit both as glide dislocations through their edge components resolved in the interface and by dislocation interactions giving rise to more efficient misfit compensators with Burgers vectors in the interface. We have been fortunate in 'catching', by TEM, the dominant interactions in flagrante delicto, and thus have a good understanding of the rearrangement processes. Hot-stage TEM experiments have been carried out to check the reactions but have not been satisfactory; the dislocations have been sluggish in their rearrangement and the devices have decomposed in the microscope.

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3. The Structure and Properties of Amorphous Alloys and their Crystallization Products

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Support: NSF/MRL
U of P
NSF

Objective and Approach: The amorphous metallic alloys constitute a most interesting material. For example, their fracture characteristics are nearer those of glasses rather than metals but unlike glass, they show deformation characteristics of metals. Our studies have shown that a predominant characteristic responsible for the amorphous alloy behavior must be the viscosity. There are, of course, many other fascinating reasons why this system of materials is of scientific interest. Our crystallization products are, themselves, of interest in the way they are transformed and in their mechanical behavior.

Progress: Mechanical behavior, deformation and fracture have been investigated for amorphous Ni-Pd-P alloys made by an improved Pond and Maddin method. The stress-strain curves of $\text{Ni}_{55}\text{Pd}_{35}\text{P}_{10}$ and $\text{Ni}_{63}\text{Pd}_{17}\text{P}_{20}$ show quasi-brittle behavior with average fracture stresses of 149 and 142 kg/mm², respectively. These stresses are high in comparison with those of normal metals and alloys. The elongations are small, 0.042 and 0.023% for $\text{Ni}_{55}\text{Pd}_{35}\text{P}_{10}$ and $\text{Ni}_{63}\text{Pd}_{17}\text{P}_{20}$, respectively, as is the elongation of all amorphous alloys. Fracture surfaces observed with a scanning electron microscope show two distinct regions, a featureless zone and one called a 'vein' or 'ridge' pattern. A suggested grease model gives a good simulation of the actual fracture morphology.

In parallel research, thickness reduction, ϵ_t and the elongation of Ni-Pd-P metallic glass up to 40 and 26 per cent can be attained in rolling. Deformation bands develop and are wavy in appearance and similar to single crystals of pure b. c. c. metals.

Observations at various stages during bending show that cracks can be created as the result of the crossing of two 'slip bands' similar to the behavior in crystalline materials.

From previous research it became apparent that the general features of the manner in which the amorphous alloys crystallized should be studied in detail. Accordingly, the crystallization of $\text{Ni}_{55}\text{Pd}_{35}\text{P}_{10}$

alloys was examined by isochronal resistivity and hardness measurements, along with observations of the phase transformation in the heating stage of a transmission electron microscope (TEM). The resistivity temperature coefficient between 26 and 250°C is low ($9.38 \times 10^{-5} \%/\text{C}$); a few metastable phases form on crystallization. The hardness-temperature curve shows the hardness to increase as the metastable phases appear.

Since there can be various stages of the crystallization we also studied the mechanical behavior of partially crystallized alloys. The samples with a few per cent crystallization show a fracture stress (175 kg mm^{-2}) and apparent Young's modulus ($19.5 \times 10^3 \text{ kg mm}^{-2}$) greater than those completely amorphous or partially crystallized 50%. On the other hand, the fracture strain of the former are lower than those of the two latter. A simulated model with mixtures of carborundum powder with grease, shows accord with morphological and mechanical aspects of the partially crystallized alloys. As expected, microcrystals embedded in an amorphous material act as obstacles to plastic flow.

During our research we noted that the electrical resistivity of the amorphous alloys could be a sensitive function of the deformation behavior. On further study there appeared to be a correlation between load extension curves and resistivity strain. We have analyzed this behavior and consider the effect to be of enough importance so that a more detailed study should be made.

The basic characteristics of the deformation of the nickel palladium phosphorus group of alloys is noted through its tensile behavior. These alloys show an inhomogeneous plastic deformation as do all other amorphous alloys. A few localized deformation bands appear macroscopically just beyond the elastic region of the stress strain curve.

In most cases, ribbon samples fracture in a plane stress condition and in an antiplane shear mechanism.

Two types of localized deformation bands can be produced during the tensile deformation, i. e., one has sharp steps which are produced by plastic flow associated with a shear, and the other has interconnecting voids similar to a crazing crack in polymers.

A detailed investigation of the crystallization of the amorphous Fe-P-C was conducted. The compositional dependence of the phase transformations in Fe-P-C alloys has been studied. Iron and phosphorus rich alloys and alloys with compositions near the eutectic line were considered. The study was carried out using transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and X-ray

diffraction (XRD) It was found that the transformation processes were dependent upon the composition of the alloy. Different phases are produced in different alloys and a simple free energy model is used to explain the results.

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4. Embrittlement of Structural Alloys by Impurities

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Support: NSF/MRL
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Objective and Approach: The overall objective of this research is to achieve a fundamental understanding of the embrittlement of structural alloys by impurities and to provide the basis for optimization of such alloys for toughness at ordinary and elevated temperatures and in aggressive environments. Elements from Groups IV to VI, the "metalloids", tend to segregate to grain boundaries in transition metals and to reduce cohesion there. This leads to a reduction in fracture toughness, often over a wide range of temperature, and to enhanced cavitation and crack growth in grain boundaries at high temperatures. This also causes an enhanced sensitivity to intergranular cracking under stress in aggressive environments, the apparent result of an interaction between metalloids and hydrogen (hydrogen-assisted cracking) and of the ability of metalloids to interfere with re-passivation after slip-induced oxide film rupture (stress corrosion cracking).

Our efforts are focused on these phenomena in alloy steels, specifically those used in power generating and fuel processing equipment. The specific objectives of this program are: (1) to determine the embrittling potency of each important metalloid element; (2) to determine how the above actions of each element are influenced by

changes in microstructural variables, such as hardness and grain size; (3) to determine the factors, such as alloy content and thermal history, which control the kinetics and equilibrium amounts of metalloid segregation (as a function of temperature).

The approach in this program involves: (1) correlation of notched-bar fracture energy with grain boundary composition, as measured by Auger electron spectroscopy; (2) measurements of grain boundary and free surface segregation of metalloids as a function of alloy content, temperature, and time; (3) measurement of effects of individual impurities on cavitation and cracking in notched bars at elevated temperatures.

Progress: We have nearly completed an investigation of the mechanism by which a special heat treatment procedure, known as intercritical heat treatment ICHT, acts to reduce susceptibility to temper embrittlement in alloy steels. (This process is currently being considered for commercial use.) In two laboratory heats doped with P and Sb, respectively, we have found that ICHT almost eliminated embrittlement susceptibility in the P-doped steel. The effect can be attributed entirely to a refinement of grain size. The rate of embrittlement was reduced significantly in the Sb-doped steel, but the amount which occurred in 1000 h ageing at 480°C was still considerable, indicating that this process will be limited utility in the presence of a strong embrittling element.

The first phase of the study of temper embrittlement in Cr-Mo steels has been completed. We have found that Sn does not embrittle a pure Cr-Mo steel; this is consistent with recent results which indicate that Ni or Mn are required for embrittlement by Sn or Sb. However, P has proved to embrittle the pure Cr-Mo steel, and the effects of hardness and grain size have been characterized.

In a preliminary study of several heats of a commercially produced nuclear pressure vessel steel (A533B) we have demonstrated that serious intergranular embrittlement occurs during a simulated welding process if the steel contains enough metalloid impurity (in this case As). This has led to the initiation of a study of this class of steel (1.5% Mn, 0.5% Mo, 0.5% Ni) to determine the safe levels of such impurities.

Perhaps the most important accomplishment in the past year is the achievement of an understanding of most of the types of alloy/metalloid interactions which can either enhance or retard metalloid segregation. As the attraction between these elements in solution in α -Fe gets stronger (i. e., as the heat of formation of the relevant alloy/metalloid compound gets more negative) the tendency for intergranular segregation increases. However, if the attraction gets strong enough,

mutual immobilization (e.g., by precipitation) occurs, and segregation then ceases.

We have also discovered another alloy element effect in which segregation of Ti to grain boundaries reduced the embrittling potency of segregated Sb. This presumably offers some clues to the physical nature of the embrittlement. We are presently examining the electron concentrations and atomic volumes of various combinations of elements to attempt to determine if these are the controlling factors.

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5. Mechanical Properties of Ordered Alloys

D. P. Pope, Associate Professor of Metallurgy and Materials Science

Postdoctoral Fellows: K. Abiko
S. Kulkarni
E. Kuramoto
C. Lall

Research Assistant: R. L. Bodnar

Support: NSF/MRL
ERDA
NSF-RANN
EPRI
JPL

Objective and Approach: Ordered alloys are playing increasingly large roles in materials technology. (The most simple ordered alloy is an A-B alloy in which the A atoms occupy certain specific lattice sites and the B atoms occupy other sites.) The ability of certain alloys to undergo large, reversible deformations, (on the order of a few percent as compared with a few tenths of a percent for normal alloys) is related to their ordered structure. Other ordered alloys are extensively used as small precipitates to strengthen bulk alloys. The aircraft aluminum alloys, the high temperature nickel base alloys and the new low carbon maraging steels are in this category.

In this program we are studying the properties of the class of alloys having the same structure as Cu_3Au (the precipitates in the maraging steels and in the nickel-base alloys also have this structure.) These alloys, almost without exception, show a strength increase with increasing temperature, just the opposite of normal alloys. We are studying these alloys with the objective of finding the cause for the observed strength anomalies (and other anomalies as well). To this end we are performing deformation experiments on single and polycrystalline samples, examining the structure of the deformed samples using electron microscopy and performing dislocation mobility experiments.

Progress: During this past year our efforts have been concentrated on performing tensile tests on Cu_3Au single crystals. These tests required the production of single crystal tensile samples, about 2" long, with controlled orientations and with provisions for being gripped in the testing machine. The successful production of these samples is certainly

major accomplishment #1. (Tests could have been performed on much smaller, less complicated compression samples, but there is always a difficulty in guaranteeing stress homogeneity in such samples.)

These samples were used to measure the yield stress and work hardening rate of Cu_3Au as a function of orientation and temperature to provide critical tests of competing theories. The yield stress experiments showed that the theory we advanced a few years ago for the strength increase with temperature of Cu_3Au is almost certainly correct. (The experiments were performed by Dr. Eiichi Kuramoto from the University of Tokyo who put forth the most widely accepted rival theory, so there is probably rather little internal bias in this statement.)

We have also shown that the very high work hardening rate of Cu_3Au , which has a maximum around room temperature, is most likely related to cross slip of screw dislocations from the (111) slip plane to (100) planes where they are immobile. This cross slip becomes increasingly easier as the temperature goes up, but we still do not understand the reason for the decrease at higher temperatures. (This behavior is compatible with Dr. Kuramoto's theory, so he didn't make the long journey only to prove that his theory is totally inapplicable to Cu_3Au .)

We have also prepared single crystalline samples of Ni_3Al that are almost ready now for dislocation mobility experiments.

Publications:

Pope, D. P. and Liang, S. J., "A Reconciliation of the Controversial Results of Microstrain Damping Experiments on Ordered and Disordered Cu_3Au ", *Scripta Met.* 10, 219 (1976)

Pope, D. P., Lim, J. Y., McMahon, C. J., Jr. and Williams, J. S., "The Effect of Oxygen on the Structure and Mechanical Behavior of Aged Ti-8 wt % Al", *Metal. Trans.* 7A, 139 (1976)

Pope, D. P. and Liang, S. J., "The Difference in Latent Hardening Effect among Li_2 Ordered Alloys", *Metal. Trans.* (Accepted)

Pope, D. P. and Kuramoto, E., "The Orientation Dependence of the Yield Stress of Cu_3Au ", *Phil. Mag.* (Accepted)

Pope, D. P. and Kuramoto, E., "The Orientation Dependence of the Work Hardening Coefficient of Cu_3Au ", *Phil. Mag.* (Accepted)

C. MOLECULAR CRYSTALS

1. Organic Metals: Synthesis of Heteroatom π -Donors and Acceptors

M. P. Cava, Professor of Chemistry

Postdoctoral Fellows: M. V. Lakshmikantham
H. K. Spencer

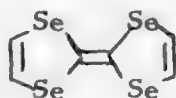
Support: NSF/MRL
NIH
NSF

Objective and Approach: Our objective is to synthesize and prepare small organic molecular units for use in highly conducting organic solids. Recent work at Penn on the metallic state properties of organic solids such as (NMP)(TCNQ) and (TTF)(TCNQ) and related derivations has provided a set of guidelines for productive synthetic studies, especially with stable organic free radicals. On the basis of our previous experience with small heteroatom organic molecules, we plan to continue a series of systematic studies to synthesize a number of TTF related stable radicals for use with TCNQ and related π -acceptors.

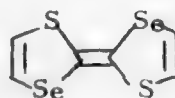
Progress:

Major Accomplishments

1. We have devised a new and practical synthesis of tetraselenafulvalene (TSeF) making this material available in quantity for complex formation with TCNQ. The direct tetradecarbomethoxylation discovered in the course of this work has been found to be of general applicability in this series. This has allowed us to vastly improve the yields in our previously reported synthesis of DSeDTF.

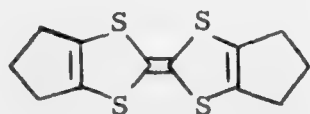


TSeF

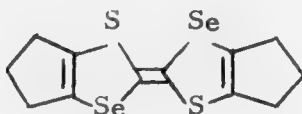
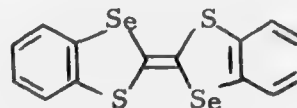


cis/trans DSeDTF

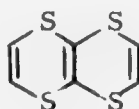
2. Several annelated TTF and DSeDTF derivatives have been synthesized. This has involved improvements to existing synthetic procedures for the intermediate compounds, such as the annelated thia-diazoles, selenadiazoles, and various thiones and selones. In addition, in the case of annelated DSeDTF derivatives a novel and practical synthetic route of general applicability was developed.



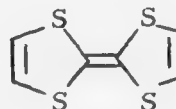
cyclopenteno TTF

cis/trans sym-
dicyclopenteno
DSeDTFcis/trans sym-
dibenzo DSeDTF

3. Tetrathiatetralin (TTL) the hitherto unknown structural isomer of TTF was synthesized. In spite of its close relationship to TTF, TTL is much less easily oxidized to a cation radical. TTL is, however, of tremendous theoretical interest.

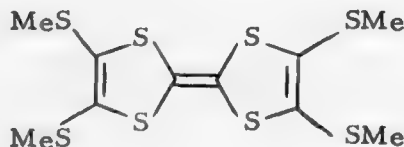


TTL



TTF

4. A greatly improved synthesis of tetrathiomethyl TTF has been achieved, making this compound easily available for further study for the first time.



All methods described are currently in use to prepare materials for solid state research at LRSM.

Presently efforts are being made to synthesize the hitherto unknown unsymmetrical TTF and DSeDTF derivatives, complexes of which with TCNQ or TNAP will be of unusual interest to the solid state physicists.

Publications:

Spencer, H. K., Lakshmikantham, M. V., Cava, M. P. and Garito, A. F., "Organic Metals: Annelated sym-Diselenadithiafulvalenes", J.C.S. Chem. Commun. 867 (1975)

Lakshmikantham, M. V. and Cava, M. P., "An Alternate Synthesis of Tetraselenafulvalene", J. Org. Chem. 41, 882 (1976)

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Mizuno, M., Cava, M. P. and Garito, A. F., "1,4,5,8-Tetrathia-tetralin, a Tetrathiafulvalene Isomer", J. Org. Chem. (in press)

2. Determination of Crystal Structures by the X-ray Diffraction Method

J. Donohue, Rhodes-Thompson Professor of Chemistry

Research Assistant: B. S. Hayward

Support: NSF/MRL
NIH

Objective and Approach: The purpose of this project is to determine the crystal structures of various substances, with the results to include precise information concerning bond distances, bond angles, torsion angles, conformations, thermal vibrations and non-bonded interactions. The substances chosen for study fall into three broad categories:

1) biologically active compounds, 2) compounds of unknown chemical structure, and 3) compounds suited for the observation of intermolecular forces.

In 1) it is important to know the structures of such materials in order to understand how they act in living systems. In 2) quite often studies of chemical reactions give products whose chemical structures are unknown. When these structures are determined by diffraction methods, only then can a complete discussion of the reactions themselves be made. In 3) the results should add to our understanding of various interactions between molecules in solids.

Progress:

1. Biologically related molecules the structures of which have been determined and/or refined include tetraphenylmethane, biotin (Vitamin H), acetoxychlorohexahydronaphthalene, diglycylcystine, aureomycin, dibucain, and dimethisoquin. The last two are local anesthetics, and attempts are being made to correlate this property with their structures as related to membrane structure.

2. Compounds of unknown chemical structure include hexadecamethylbicyclononasilane and sulfur nitride polymer. In the first a new silicon cage framework was found.

3. Our work on intermolecular forces in crystals includes examination of the numerous forms of elemental sulfur, and various sulfur-nitrogen-hydrogen compounds. This work is only at an early stage of development.

Publications:

Robbins, A., Jeffrey, G. A., Chesick, J. P., Donohue, J., Cotton, F. A., Frenz, B. A. and Murillo, C. A., "A Refinement of the Crystal Structure of Tetraphenylmethane: Three Independent Redeterminations", *Acta Cryst.* B31, 2395 (1975)

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Boggs, R. and Donohue, J., "Trans 4a-acetoxy-8a-chloro-1,4,4a,5,8,8a-hexahydronaphthalene", *Acta Cryst.* B32, 1918 (1976)

Stallings, W. and Donohue, J., "Refinement of N,N'-diglycylcystine", *Acta Cryst.* (in press)

3. Theory of Electric and Magnetic Properties of Molecules

H. F. Hameka, Professor of Chemistry

Research Assistant: L. V. Haley

Support: NSF/MRL

Objective and Approach: Our main efforts are directed towards a theoretical description of the electric polarizabilities and dipole moments of molecules. The ultimate goal is to correlate the values of the polarizabilities with the chemical structure of molecules. Initially we are developing various theoretical approaches and we are testing them out on small molecules. We hope that the results of such calculations will enable us to recognize which effects are important contributions so that we will be able to construct a semi-empirical theory that applies to a variety of molecules.

Progress: The research that was outlined in the research proposal for 1975-1976 was successfully implemented.

Publications:

Hameka, H. F. and Svendsen, E. Nørby, "Errors in the Calculation of First-Order and Second-Order Energy Perturbations", *Intl. J. of Quantum Chem.* 10, 249 (1976)

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4. Studies of Highly Conducting Organic and Polymeric Solids

A. J. Heeger, Professor of Physics

A. F. Garito, Associate Professor of Physics

Postdoctoral Fellows: C. K. Chiang
M. J. Cohen
L. B. Coleman
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Research Assistants: C. R. Fincher
W. J. Gunning
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Technicians: K. Desai
P. S. Kalyanaraman
P. J. Nigrey

Support: NSF/MRL
ARPA
NSF
U of P

Objective and Approach: Our objective is to develop a new class of materials composed of organic, or inorganic molecules with the eventual goal of technologically utilizing these materials for their anisotropic electronic properties. The reason for the interest in these materials is the attractive feature that they are chemically synthesized from flat planar, or linear molecules which lead to anisotropic structures and pseudo one-dimensional electronic properties. We have successfully synthesized organic metals characterized by excess conductivity resulting from collective many body phenomena in one-dimensional conductors, and prepared the first oriented epitaxial films of a metallic polymer. The work is interdisciplinary and involves a back-and-forth interplay between chemical synthesis and broad-based experimental and theoretical physical studies. The overall goal is to create solid state materials with a desired bulk property by preliminary design of constituent molecules.

Progress: Work during this period centered on three problems:

I. The one-dimensional organic metal TTF-TCNQ and related derivative salts.

II. The first metallic polymer; polymeric sulfur nitride, $(\text{SN})_x$.

III. The Spin-Peierls Transition.

I. Organic Metals: TTF-TCNQ and Related Salts

Our earlier studies of the dc, microwave, and optical properties of TTF-TCNQ showed that in the high temperature conducting state above 58 K, there is an energy gap at $\hbar\omega_g = 0.14$ eV and an extremely narrow conductivity mode centered at zero frequency. Near 58 K, TTF-TCNQ undergoes a metal-insulator transition to a high dielectric constant semiconductor state in which the oscillator strength is shifted from zero frequency and pinned in the far infrared.

We proposed earlier that these phenomena are associated with a collective many body condensation of the conduction electrons into a Peierls-Fröhlich charge density wave (CDW) state accompanied by a periodic lattice distortion. Our experimental studies suggest TTF-TCNQ provides the first example of collective many body electronic transport by CDW condensation.

A. Direct Observation of Peierls Distortion and Giant Kohn Anomaly by X-ray Diffuse Scattering and Elastic and Inelastic Neutron Scattering. The direct observation and study of the structural superlattice in TTF-TCNQ at temperatures below 54 K was a turning point in the field. The successful observation of the superlattice confirmed the existence of the Peierls instability as originally proposed by us more than three years ago.

B. Microwave Conductivity: The microwave conductivity studies for TTF-TCNQ were published based on the completion of a theory of the microwave losses of one-dimensional conductors in the skin effect regime. The results are in good agreement with the earlier dc results and indicate peak normalized conductivities between 50 and 100 with intrinsic absolute values of approximately $5 \times 10^4 \Omega^{-1} \cdot \text{cm}^{-1}$ at 58 K.

C. Far Infrared Studies: Far infrared studies (10 cm^{-1} to 100 cm^{-1}) on single crystal samples confirmed the existence of the energy gap and yielded a quantitative measure on the residual conductivity in the gap region.

D. Knight Shift Studies: The temperature dependence of the C^{13} Knight shift and spin lattice relaxation rate labeled at the CN group of TCNQ were used to investigate the local susceptibility and strength of electron-electron interactions in TTF-TCNQ. The temperature dependence of the TCNQ chain susceptibility is in quantitative agreement with the calculated susceptibility based on the Peierls-Fröhlich model with complex order parameter.

E. Studies of Derivative Salts: Studies of related derivative salts, TMTTF-TCNQ, DTDSeF-TCNQ, and TSeF-TCNQ, indicate that a common mechanism is involved in this class of one dimensional conductors. The remarkably large low temperature b-axis dielectric constant, $\epsilon_1 \geq 3000$, originally discovered by our group has now been observed in all these compounds.

II. Polymeric Metals: $(SN)_x$

We determined from x-ray results, the detailed mechanism for the solid state polymerization of S_2N_2 to $(SN)_x$; filed two patent applications for the first known example of oriented epitaxial film growth of any polymer; and showed from conductivity, optical, and inelastic electron energy-loss studies that $(SN)_x$ is not a 1 D conductor but a 3 D semimetal.

Measurements of the b-axis electrical conductivity of polymeric sulfur-nitride, $(SN)_x$, from 4.2 K to 300 K were reported for samples having different polymerization times. A general increase in the conductivity was found with longer polymerization times leading to room temperature conductivities of $1200 - 3700 (\Omega\text{-cm})^{-1}$, conductivity ratios $(\sigma(4.2 \text{ K})/\sigma(300 \text{ K}))$ of 50-205, and the temperature dependence of the resistivity following a T^2 form. This work was carried out in collaboration with Alan MacDiarmid (Chemistry).

III. The Spin-Peierls Transition

Studies of the spin-Peierls transition in TTF-BDT(M), $M = \text{Cu}$ and Au , were carried out to investigate the nature of this transition of the spin- $\frac{1}{2}$ one-dimensional (1 D) Heisenberg chain. Nuclear relaxation results agreed in magnitude, frequency dependence and temperature dependence with calculations based on the pseudofermion treatment. The specific heat results demonstrated the linear term, γT , expected for the uniform (1 D) chain above the Peierls transition with specific heat anomalies at $T_p(\text{Cu}) = 12.4 \text{ K}$ and $T_p(\text{Au}) = 2.06 \text{ K}$. The transition for TTF-BDT(Cu) is mean field like; whereas, the transition for TTF-BDT(Au) is broadened by 1 D fluctuation effects.

Publications:

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5. Electronic Structure and Relaxation Processes in Molecular Crystals

R. M. Hochstrasser, Blanchard Professor of Chemistry

Postdoctoral Fellows: I. Abram
R. G. Bray
D. L. Narva
A. C. Nelson

Research Assistants: R. W. Anderson, Jr.
J. M. Friedman
D. S. King
C. M. Klimcak
F. A. Novak
C. A. Nyi
H-N Sung

Support: NSF/MRL
NIH
AROD
NSF
USA
U of P

Objective and Approach: In this research we try to understand in a fundamental way dynamical processes that occur in molecular crystals, especially those processes that are optically induced. In addition we are exploring for novel properties of this class of materials using a number of laser techniques. So the research is devoted to understanding better the properties of many different types of molecular aggregates and using our knowledge of their states, optical properties and relaxation mechanisms to generate new laser systems and materials.

Besides our interest in how molecules in crystals transfer or redistribute their internal energy and how such excitations lose their mutual coherence, we are also interested in the mechanisms of relaxation that lead to chemical reaction. It turns out that molecular crystal sites can topologically control the course of chemical reactions. Molecular crystals are in reality alloys because of the presence of isotopes in natural abundance, and another of our interests is to explore isotopically selective photoprocesses. This study has an immediate practical goal of providing new methods for isotope separation.

A continuing objective of this research involves the development of techniques for studying properties of crystal and molecular states.

These techniques in turn often expose new properties of the materials. For many years now we have attempted to probe for very small numbers of molecules and our present limit of ca. 10^6 molecules per cm. of travel of the light, while not the ultimate goal, already signals uses for our techniques in other fields such as in the study of surfaces.

Using our linear chain exciton system (1,4-dibromonaphthalene) we have completed experiments that expose the mechanism of energy transfer even in heavily isotopically mixed crystals. These experiments involve detecting exciton collisions by modulating the delayed luminescence (resulting from exciton annihilation) by means of a microwave field in resonance with the exciton fine-structure levels. We have discovered that the excitation energy is transported through the crystal by rapidly jumping between defect sites at which it spends the largest fraction of its lifetime. Such effects, even in the purest crystals yet made, mainly determine the loss of coherence amongst excitons.

We have managed to carry out a clean photochemical reaction in a molecular crystal at 1.6 K. An aromatic (tetrazine) absorbs green light and produces one N_2 and two HCN molecules for every absorbed photon. We have carried out this reaction with tetrazine dispersed in a crystal of benzene, and when a narrow band dye laser is used it was possible to photo-select molecules containing carbon-13, nitrogen-15 or hydrogen-2 and thereby effect 100% isotope separations on a small scale.

We have made a detailed study of the dynamics of excitation energy transfer between two molecules interconnected by a chemical bond. In the system (naphthalene)- CH_2 - (benzophenone) we have excited the ketone part with a 6 ps light pulse and made observations of the spectra of the system over the period 0 to 20 ps, during which time the energy redistribution can be seen directly.

By means of transient optically detected magnetic resonance we have delineated key features of an impurity center in a molecular crystal. The impurity states lie above the bands and therefore have not been amenable to study by conventional means. The ability of a single impurity molecule to distort the structure and modify the electronic properties of a molecular crystal is an important feature of these materials.

Recent progress in techniques includes our observation for the first time of a three photon spectrum of a crystal. The crystal simultaneously interacts with three photons from a dye laser (frequency ω) to cause a transition between states separated in energy by $3\hbar\omega$. Novel momentum selection rules are involved so new band states can be reached. So far only crystals of aromatic molecules have been used in these experiments.

We have made great progress with the picosecond laser system in understanding fast processes in molecular systems. We have been able to observe spectral and fluorescence changes in an accurate manner using a newly designed spectrometer that responds to a single laser pulse, providing a complete spectrum of any transients and their time dependence. Using this apparatus we have studied and characterized a new type of long-range energy transfer that occurs from unrelaxed states of condensed systems. We have studied the molecular fragments that are produced following photodissociation of tetraphenylhydrazine and have found that the otherwise reactive free radicals do not recombine within a few tens of picoseconds after their formation. This apparatus has been used to study the photoexcited tetrazine molecules prior to their isotopically sensitive predissociation. We now know that the predissociation takes 300 ps and is an exponential decay.

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Hochstrasser, R. M. and Nelson, A. C., "A Study of Energy Transfer between Electronically Excited States using a Picosecond Laser Pulse", Optics Comms. (in press)

6. Synthesis and Study of Organometallic and Polymeric Metallic Conductors

A. G. MacDiarmid, Professor of Chemistry

Postdoctoral Fellows: M. Akhtar
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E. J. Louis
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Research Assistant: M. J. Moran

Support: NSF/MRL
NSF
ONR
NATO

Objective and Approach: The objective of this research is to synthesize and study new inorganic and organometallic materials which might exhibit, or might be expected to exhibit, novel electrical or magnetic properties. It is believed that, for the continued active growth of materials science, it is necessary to have a vigorous program involving the synthesis of new types of substances. Exciting, important, "Quantum-jumps" occur when new substances with unexpected, scientifically or technologically important properties are discovered.

The broad objective of this investigation is to synthesize and study new chemical compounds which behave as metals. Of particular, but not exclusive, interest are polymers which are metals, even though they contain no metal atoms. The first example of such a polymer, the remarkable compound, polymeric sulfur nitride $(\text{SN})_x$, was synthesized for the first time in the form of pure golden crystals in this laboratory two years ago. It is believed $(\text{SN})_x$ may be the forerunner of a whole new class of inorganic "polymeric metals" based on diatomic neutral, cationic or anionic monomeric units containing one unpaired electron, isoelectronic with $(\text{SN})_x$. The synthesis and study of such compounds will be undertaken.

Progress: Research has proceeded very satisfactorily during the past twelve months. Major accomplishments are listed below:

(1) Detailed studies on the chemical stability of pure, crystalline $(\text{SN})_x$ towards air, dry oxygen (1 atm. pressure), moist oxygen (1 atm. pressure) and water vapor have been performed. It has been demonstrated

conclusively that completely polymerized $(\text{SN})_x$ undergoes no detectable reaction with the above gases during 1 week at room temperature; however, if the $(\text{SN})_x$ contains any unpolymerized dimer, S_2N_2 , the material reacts readily with air.

(2) A full study of the crystal structures of S_3N_2 and $(\text{SN})_x$ and the mode of solid state polymerization of S_2N_2 to $(\text{SN})_x$ has been completed.

(3) The conductivity of crystals of $(\text{SN})_x$ has been studied as a function of polymerization time (after removal of any unpolymerized S_2N_2). The polymerization time ranged from hours to several weeks. It was most interesting to find that as polymerization time increased: (a) the conductivity increased markedly, (b) the extent to which the conductivity increased with a decrease in temperature increased, (c) the maximum in the $\sigma_T/\sigma_{300\text{K}}$ ratio moved to lower temperatures and became more pronounced.

(4) It has been shown that the solid state polymerization of S_2N_2 to $(\text{SN})_x$ proceeds via a free radical process which commences at the surface of the S_2N_2 crystals. The S_2N_2 at first changes from colorless, diamagnetic crystals to black paramagnetic crystals ($g = 2.005$) and then to golden, diamagnetic crystals of $(\text{SN})_x$. Polymerization is inhibited by free radical scavengers.

(5) It has been shown that when $(\text{SN})_x$ is vaporized at approximately 145°C the only observable neutral gaseous species is $(\text{SN})_4$, a very reactive isomer of S_4N_4 which deposits golden, crystalline films of $(\text{SN})_x$ on room temperature surfaces of glass, metals or polymer.

(6) It has been demonstrated that when S_4N_4 vapor is passed over heated quartz or Pyrex wool at approximately 175°C it is converted to a very reactive species (possibly $(\text{SN})_4$) which deposits aligned epitaxial films of $(\text{SN})_x$ on oriented plastic surfaces at room temperature. This is a major advancement in $(\text{SN})_x$ chemistry, since it gives a reproducible way of preparing $(\text{SN})_x$ directly from S_4N_4 , without having to first synthesize S_2N_2 and then polymerize it in the solid state to $(\text{SN})_x$.

(7) Preliminary evidence has been obtained which strongly suggests that, surprisingly, the formation of aligned epitaxial films of $(\text{SN})_x$ on a polymer surface from $(\text{SN})_4$ vapor is determined, at least in some instances, by the microscopic properties of the surface, rather than by the molecular unit cell dimensions of the polymer.

(8) Mass spectral studies have shown that $(\text{SN})_x$, as commonly synthesized, contains from 1 to 5 atom percent of hydrogen. This is an exceedingly interesting observation, and work is now continuing in order to ascertain the source of the hydrogen and its effect on the physical properties of $(\text{SN})_x$.

(9) Preliminary experiments suggest it might be possible to grow a new crystal form of $(\text{SN})_x$ from solutions of S_2N_2 .

(10) A blue-black amorphous form of $(\text{SN})_x$, which is paramagnetic and slowly converts to the golden metallic form, has been isolated.

(11) Preliminary studies strongly suggest that the first member of a new class of conducting polymer, "polymeric polysulfur nitride", $(\text{S}_y\text{N})_x$, has been isolated as a black powder of composition $(\text{S}_{1.73}\text{N})_x$. The first member of this series ($y = 1$) is $(\text{SN})_x$.

(12) Large single golden-silver crystals of the new metal, $\text{Hg}_{2.88}\text{AsF}_8$, first prepared by R. Gillespie as small crystals, have been synthesized. Single crystals up to 20 mm x 20 mm x 2 mm have been grown and their electrical conductivity and specific heat have been measured as a function of temperature.

(13) Silvery sheets of polyacetylene, $(\text{CH})_x$, have been synthesized both -78°C and at room temperature.

Research is continuing actively in the areas 6-13, inclusive, as outlined above.

Publications:

Chen, C. H., Silcox, J., Garito, A. F., Heeger, A. J. and MacDiarmid, A. G., "Plasmon Dispersion and Anisotropy in Polymeric Sulfur Nitride, $(\text{SN})_x$ ", *Phys. Rev. Lett.* **36**, 525 (1976)

Chiang, C. K., Cohen, M. J., Garito, A. F., Heeger, A. J., Mikulski, C. M. and MacDiarmid, A. G., "Electrical Conductivity of Polymeric Sulfur-Nitride", *Solid State Commun.* **18**, 1451 (1976)

Cohen, M. J., Garito, A. F., Heeger, A. J., MacDiarmid, A. G., Mikulski, C. M., Saran, M. S. and Kleppinger, J., "Solid State Polymerization of S_2N_2 to $(\text{SN})_x$ ", *J. Amer. Chem. Soc.* **98**:13, 3844 (1976)

Mikulski, C. M., MacDiarmid, A. G., Garito, A. F. and Heeger, A. J., "Stability of Polymeric Sulfur Nitride, $(\text{SN})_x$ to Air, Oxygen and Water Vapor", *Inorg. Chem.* (in press)

Smith, R. D., Wyatt, J. R., DeCorpo, J. J., Saalfeld, F. E., Moran, M. J. and MacDiarmid, A. G., "Identification of the Vapor Phase Species of $(\text{SN})_x$ ", *Chem. Phys. Lett.* (in press)

Smith, R. D., Wyatt, J. R., DeCorpo, J. J., Saalfeld, F. E., Moran, M. J. and MacDiarmid, A. G., "A Study of the Vapor Phase Species of $(\text{SN})_x$ ", J. Amer. Chem. Soc. (in press)

Louis, E. J., MacDiarmid, A. G., Garito, A. F. and Heeger, A. J., "Formation of Crystalline Epitaxial Films of the Metallic Polymer, $(\text{SN})_x$, by the Thermal Decomposition of S_4N_4 Vapour", Chem. Commun. 218, 426 (1976)

MacDiarmid, A. G., Mikulski, C. M., Saran, M. S., Russo, P. J., Cohen, M. J., Bright, A. A., Garito, A. F. and Heeger, A. J., "Synthesis and Selected Properties of Polymeric Sulfur Nitride, (Polythiazyl), $(\text{SN})_x$ ", Advances in Chemistry Series, No. 150, Ed., R. B. King, 63 (1976)

7. Laser Induced Selective Photochemical Reactions in Molecular Crystals

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Research Assistant: R. K. Dieter

Support: NSF/MRL
 RC
 PRF
 NSF
 NIH

Objective and Approach: The objective here is a study of laser-induced photochemical processes in organic molecular crystals. Our program is primarily concerned with the development of photochemical reactions which, when combined with the selectivity of lasers, will permit isotope separation. Specifically, we are examining feasible condensed phase photochemical systems that can be arranged such that upon isotopically selective excitation and prior to relaxation or energy transfer, a photochemical reaction will occur. These considerations will bring us to consider a number of new solid state physical and chemical processes, such as: a) energy transfer between isotopically related molecules in solids; b) topological aspects of chemical reactions in molecular crystals; and c) the effects of temperature on thermal and photochemical reactions in the crystalline state. Concomitant with this study of solid state photochemistry there is ample opportunity to devise reaction schemes which could be used in isotope separation. Through this effort we hope to provide new means for obtaining energy rich material for the application of isotopes in chemical research and technology. In addition, there is an obvious need for the development of new sources of light atom isotopes in biomedical research for use as tracers. An important aspect of the present study is the extremely low temperatures at which the photochemical reactions will be explored. Thus it will be possible to study unstable intermediates as well as design reaction pathways unique to the solid state.

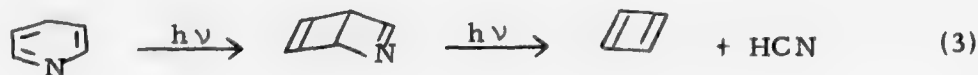
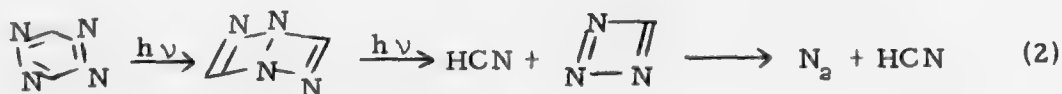
During the past 10 years certain principles regarding the nature of condensed phase spectra have been delineated. Most important among these is the fact that the lowest energy electronic transition will provide a sharp vibronic spectrum, the width of which is determined by the largest of two factors - the inherent linewidth and the broadening due to the inhomogeneity of the sample. Whenever both of these factors are less than the energy separation between transitions for isotopically related molecules, it will be possible to selectively excite these groups

of molecules. Then with the appropriate prearranged topology in the neat or mixed crystal it should be quite feasible to chemically trap the isotopically selective excited species.

Progress: During the past year our research has centered primarily on the low temperature photochemistry of *s*-tetrazine and related derivatives in molecular crystals. We describe here in some detail several of these ongoing projects.

s-Tetrazine and its Photochemical Decomposition

The recent observation by Hochstrasser and King that *s*-tetrazine in neat or mixed crystal systems undergoes isotopically selective photochemical decomposition from either the $n-\pi^*$ singlet ($^1B_{3u}$) or triplet ($^3B_{3u}$) to yield two equivalents of HCN and one equivalent of N_2 , has led us to initiate a mechanistic study of this interesting reaction. Two possible reaction pathways are immediately discernable. First, excitation could lead to a concerted fragmentation of *s*-tetrazine yielding directly N_2 and HCN. On the other hand, excitation could lead to a "dewar benzene-like" intermediate which via subsequent elimination of HCN would yield the interesting tri-azacyclobutadiene. Decomposition of this intermediate would then lead to N_2 and a second equivalent (eq.) of HCN. These reaction pathways are illustrated in equations (1) and (2) below)



The recent observation (equation 3) of azadewar benzene and cyclobutadiene arising from the photochemical decomposition of pyridine (8°K , argon matrix) provides good precedent for pathway (2) above. [O. Chapman et al., J. Amer. Chem. Soc. 95, 614 (1973)].

To distinguish between these alternative pathways we are currently developing a stereospecific synthetic scheme to *s*-tetrazine labeled with N^{15} at both the 1 and 4 positions. Photochemical decomposition of such a material via either pathway (1) or (2) will yield 1 eq. of HCN (mw 27) and 1 eq. HCN (mw 29). On the other hand, the resultant nitrogen from pathway (1) will be entirely N_2 (mw 29), while pathway (2) will yield an isotopic mixture of N_2 : $\frac{1}{4}$ eq. N_2 (mw 28), $\frac{1}{2}$ eq. N_2 (mw 29) and $\frac{1}{4}$ eq. N_2 (mw 30). Thus by high resolution mass spectrometric monitoring of the resultant N_2 it should be relatively straightforward to discern which pathway is followed in the photochemical decomposition of *s*-tetrazine.

Photochemical Decomposition of Related *s*-Tetrazine Derivatives

In addition to our mechanistic studies on *s*-tetrazine we are currently exploring the low temperature photochemistry of dimethyltetrazine and phenyl-tetrazine in neat and mixed crystals. As with *s*-tetrazine these derivatives undergo similar photochemical fragmentation reactions leading to N_2 and 2 eq. CH_3CN in the case of dimethyltetrazine and N_2 , HCN and benzonitrile from phenyltetrazine. In addition, Hochstrasser and King have recently devised a molecular crystal system wherein it is possible to optically resolve the various isotopic species of phenyl-tetrazine. With these observations in hand it now appears quite feasible to prepare μg to mg quantities of benzonitrile- N^{15} ($> 95\% N^{15}$) from natural abundance phenyltetrazine.

Finally, work is currently in progress directed at the preparation of 1-naphthyl and 9-anthracenyl tetrazine which will allow us to explore in greater detail the photophysics of the tetrazine decomposition reaction.

Publications:

Smith, A. B., III and Dieter, R. K., "Intermolecular Photochemical Oxetane Formation in Two $\beta, \gamma-\gamma', \delta'$ -Diunsaturated Ketones", *Tetrahedron Letters* 327 (1976)

8. Synthesis and Studies of Mixed Valence Compounds

L. G. Sneddon, Assistant Professor of Chemistry

Research Assistant: M. Freeman

Support: NSF/MRL
RC
KCC

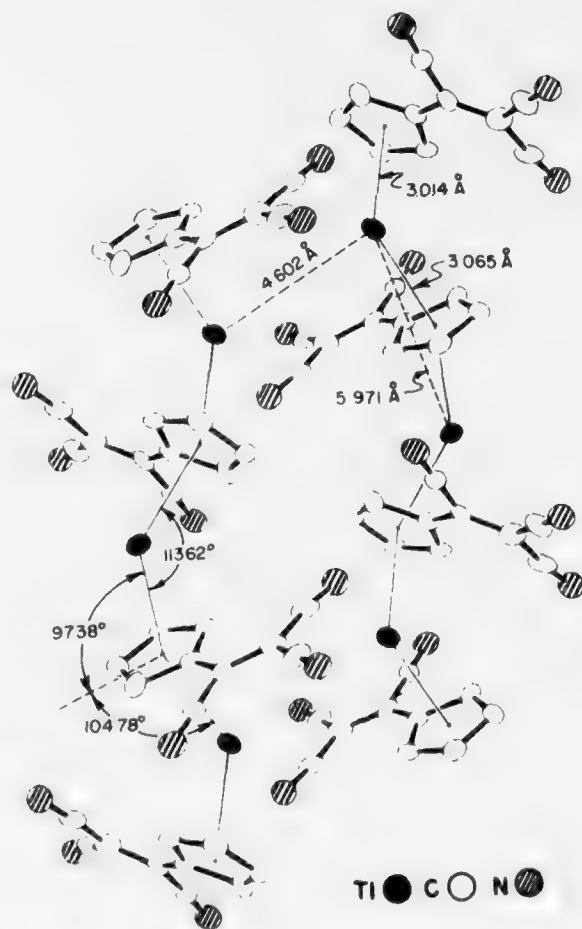
Objective and Approach: Mixed valence inorganic compounds have been shown to have a number of unique physical and chemical properties. These properties range from color, magnetism and solid state conductivity to chemical reactivity. Recently mixed valence organometallic compounds have received an increased amount of attention. Most of the work has centered around biferrocenes, bis-fulvalene iron and cobalt complexes and ferrocene polymers. In every case, once these compounds were converted to the mixed valence state, a dramatic increase in the electrical conductivity was observed. By combining the synthetic possibilities of organometallic chemistry with the concepts developed in solid state physics, we are attempting to synthesize new mixed valence organometallic compounds which may exhibit a variety of electrical properties (semiconducting, conducting and superconducting).

Progress: In the gas phase cyclopentadienyl thallium(I), C_5H_5Tl , and cyclopentadienyl indium(I), C_5H_5In , consist of discrete molecules having five-fold symmetry, the metal atoms lying over the rings to form a half sandwich structure. In the solid state, however, both compounds have been shown to be linear zig-zag polymers of alternating metal and cyclopentadienyl ions. For C_5H_5In the metal-to-ring distance is 3.19 Å and the metal-metal distance is 3.99 Å, which is small enough to allow the possibility of some electronic interaction. Partial oxidation of a pseudo-one dimensional stack such as TlC_5H_5 , by electron acceptors such as TCNE or TCNQ, could lead to a Tl(I)-Tl(III) mixed valence polymer associated with stacks of TCNQ or TCNE anions.

We investigated this possibility and discovered that when TCNE and TlC_5H_5 were mixed in the solid phase a golden-red material was produced which we initially believed was the mixed valence polymer. We later developed an alternate preparation of this material in solution which enabled the production of large quantities of pure material. Spectroscopic characterization and elemental analysis revealed, however, that this compound was not the mixed valence polymer, but rather the previously unknown compound, tricyanovinylcyclopentadienyl thallium. In addition, measurements of the solid state conductivity of this material indicated only poor conduction properties.

A single crystal X-ray study of this material was undertaken in collaboration with Dr. J. C. Huffman of Indiana University. The structure determination revealed (see figure) that the compound has retained a pseudo one-dimensional polymeric structure similar to cyclopentadienyl thallium and consists of parallel stacks of alternating tricyanovinylcyclopentadienyl groups and thallium atoms.

In spite of its polymeric nature in the solid state, solution conductivity measurements indicate that the compound is ionized in solvents such as DMF and acetone. This discovery suggested that we might be able to use this material as a general reagent for producing organometallic compounds containing the tricyanovinylcyclopentadienyl group. Preliminary reactions have indicated that this is the case. For example, the reaction of this material with $(C_6H_5)_3Fe(CO)_2I$ has resulted in the preparation of tricyanovinyl-substituted ferrocene.



Publications:

Sneddon, L. G. and Voet, D., "Crystal and Molecular Structure of 2-(η -cyclopentadienyl)-2-cobalta-nido-pentaborane(9)", Chem. Commun. 118 (1976)

Plotkin, J. S. and Sneddon, L. G., "Photochemical Synthesis of Coupled Carboranes and Boranes", Chem. Commun. 95 (1976)

9. Spectroscopic Studies of Molecular Relaxation in Condensed Media

M. R. Topp, Assistant Professor of Chemistry

Research Assistant: H-B. Lin

Support: NSF/MRL
Sloan Fdn.

Objective and Approach: The study of the effects of molecular environment on molecular energy dissipation is one of the more important applications of Chemical Physics in Materials Science. Our research, which uses pulsed lasers, studies the lifetimes and properties of electronically excited molecules in condensed media, in particular excited states with low fluorescence quantum-yields.

To study short-range interactions in liquids and solids, we must use special methods, since characteristic relaxation times lie in the range 10^{-12} - 10^{-14} sec. Most of the experimental techniques have been developed in our own laboratory. Our approach emphasizes fluorescence analysis and absorption saturation as opposed to transient absorption spectroscopy and Raman methods. Since fluorescence originating from very short-lived states precedes relaxation, the fluorescence spectrum and quantum-yield can be used to identify the sequence and duration of state populations in complex systems.

We are currently concerned with applying our techniques to simple aromatic molecules for ease of comparison with existing experimental and theoretical data. The first systems studied were chosen to match the laser output, but recent experimental developments have lifted this restriction. Our methods allow the study of subtle changes in fluorescence spectra, and we propose to study the influence of isotope effects, other molecular substitution and the dependence of the lifetimes and energy levels of short-lived states on pH and solvent-solute interactions.

We propose to use fluorescence quenching of subpicosecond states to study short-range energy transfer in concentrated solutions and mixed molecular crystals. This approach promises a wealth of new information in view of the estimated time-resolution of 10^{-14} sec.

Progress:

(a) Low Quantum-Yield Fluorescence

We have detected low quantum-yield fluorescence from rapidly relaxing electronic states following consecutive two-photon excitation.

We have shown that the ultraviolet spectra so obtained exhibit a dependence on the frequency, timing and intensity of irradiation pulses. The origins of this dependence lie in the presence of many states having similar decay times and fluorescence probabilities.

We have shown that picosecond irradiation of Rhodamines 6G and B yielded ultraviolet fluorescence spectra sensitive to pulse synchronization and frequency. We have interpreted these results in terms of Franck-Condon levels having subpicosecond relaxation times.

The intensity dependence is clearly demonstrated as follows:

High irradiation intensities due to the picosecond pulsed laser increase the probability for simultaneous, two photon excitation of trace impurities. Therefore, experiments were also carried out using a flashlamp-pumped dye laser such that the peak intensity of the dye laser was about 3 orders of magnitude smaller than for picosecond irradiation, the nanosecond-integrated intensities being about the same. This proved ideal for selection against simultaneous two-photon excitation. Repetition of earlier experiments showed both enhancement of the measurement accuracy for low-quantum-yield spectra and suppression of certain bands previously identified as due to trace impurity. Such improvements determine the accuracy of quantum yields which we propose to use as control parameters for future energy-transfer experiments.

We have used these methods to identify clearly the $S_2 \rightarrow S_0$ emission spectrum of rubrene in the presence of 10% of an intensely fluorescent photoproduct.

Tunable dye laser irradiation will be used to generate consecutive two-photon excitation spectra as a tracer for ultrafast, short-range energy transfer experiments.

(b) Triplet-Triplet Absorption Saturation

Since there is no analogous luminescence method to the above for triplet state relaxation methods, we have applied absorption saturation methods to study subpicosecond upper triplet state relaxation.

In a preliminary study, we have observed absorption saturation of 1,2,5,6 dibenzanthracene, finding two types of behavior. Irradiation by individual pulses caused some absorption saturation, from which we have measured an approximate rate constant of the rate determining step in triplet relaxation to be $> 10^{12} \text{ sec}^{-1}$. Further, we observed about $\sim 0.5\%$ irreversible loss of triplet state per photon incident. We are currently investigating the loss mechanism.

With our new synchronized dye laser equipment, we propose to extend these studies to similar molecules in liquid and gaseous phases to determine the irradiation-frequency dependence of both upper triplet relaxation and lowest triplet deactivation. Through these experiments we propose to study consecutive two-photon photoionization and inter-system crossing efficiencies of highly-excited states.

(c) Photoproduct Fluorescence Excitation

We have determined that the luminescence produced by intense irradiation of alcoholic solutions of benzophenone originates in a radical photoproduct. We have determined that the radical generation process can be followed at high sensitivity using fluorescence excitation. This allows an accurate study of short-range selective interactions between highly reactive molecules trapped by solvent structure.

It is an experimental fact that few simple molecules have fluorescence decay times in the range 10^{-11} - 10^{-9} sec, and this imposes a serious restriction on the time-resolution or control of relaxation rates directly influenced by solvent motion. Radicals derived from carbonyl compounds, such as benzophenone ketyl and chloranil semiquinone promise to allow the direct study of such "intermediate" relaxation processes.

(d) Laser Stabilization

It proved necessary to stabilize the output from our mode-locked laser source such that background (i. e., nanosecond-duration) laser emission was suppressed, the output profile was rendered spatially homogeneous, the durations of individual pulses were stabilized and that long trains (i. e., > 500 nsec) of intense pulses could be obtained with high reproducibility. We achieved this using an intracavity telescope via the selection of a low-order transverse mode. We have obtained strong evidence that threshold plasma formation controlled both the peak intensity and pulse duration.

Publications:

Topp, M. R. and Orner, G. C., "Group Dispersion Effects in Picosecond Spectroscopy: Frequency Dispersion", Chem. Phys. Lett. 32, 407 (1975)

Orner, G. C. and Topp, M. R., "Biphotonic Excitation of Upper State Fluorescence from Rhodamine 6G", Chem. Phys. Lett. 36, 295 (1975)

Topp, M. R., "Biphotonic Laser Excitation of the Fluorescence of Benzophenone Ketyl", Chem. Phys. Lett. (in press)

10. The X-Ray Crystal Structures of Organic Semiconductors and Metals

D. H. Voet, Associate Professor of Chemistry

Postdoctoral Fellows: G. J. Bunick
F. E. Scarbrough

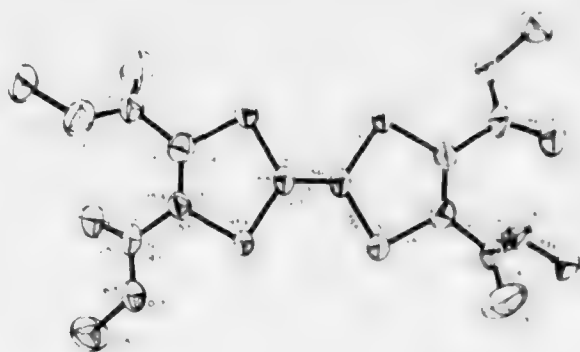
Research Assistants: G. P. McKenna
E. Uberbacher

Support: NSF/MRL
NIH

Objective and Approach: A major field of investigation under the LRSM's Molecular Crystals thrust area is that of the electrical conductance properties of charge-transfer salts. Both the positive and the negative ions of these salts consist of conjugated heterocyclic molecules. If the component ions of a crystal of such a salt have electronic properties that are properly matched and if these ions have the correct geometrical relationship, then the electrical conductance characteristics of the crystal will be that of a semiconductor or even that of a metal.

We are investigating the structures of the component molecules of these high conductance substances by single crystal X-ray diffraction analysis. This technique directly visualizes the atomic structure of a crystal. Therefore it will permit the unambiguous chemical identification of the molecules in a crystal. Of greater importance to this project, however, is that X-ray diffraction techniques reveal the conformations of molecules in a crystal together with their precise geometrical relationships with neighboring molecules. Such structural information, when correlated with data concerning the electronic properties of the salt, leads to a greater understanding of the nature of the conducting state in crystalline charge-transfer salts. This in turn should lead to the design of such materials with optimized properties.

Progress: We have completed the x-ray crystallographic determination of the TTF derivative tetracarbomethoxytetrathiafulvalene (TCMTTF). This compound, which was synthesized and crystallized by M. V. Lakshmikantham and M. P. Cava, crystallizes in the space group $P\bar{1}$ with one centrosymmetric molecule in the unit cell. The structure was solved using the heavy atom technique and refined to a final R - factor of 0.071. A drawing of the molecule is shown below. Comparison of the structure of TCMTTF with those of other TTF derivatives whose structures have been determined indicates that there is no discernable trend of covalent bonding parameters of TTF derivatives with the formal charge of the TTF nucleus.



An ORTEP drawing (Johnson, 1965) of a molecule of TCMITl indicating the covalent bond distances and angles together with the atomic numbering scheme used in this report. The molecule lies across a crystallographic center of symmetry. Thermal ellipsoids are drawn at the 50% level.

Professor Cava and Dr. Lakshmikantham have also provided us with crystals of sym-diselenadithiafulvalene. This compound crystallizes in the acentric space group P1 with 4 molecules in the unit cell. The x-ray data of this crystal have been measured and we are presently in the process of solving the crystal structure. NMR spectra of sym-diselenadithiafulvalene solutions indicate that the molecules are present in approximately equal amounts of the cis and trans isomers. The apparent complexity of the diselenodithiofulvalene unit cell suggests that a similar mixture of isomers will be found in the crystal structure.

Publications:

Belsky, V. K. and Voet, D., "Tetracarbomethoxytetrathiofulvalene", *Acta Cryst.* B32, 272 (1976)

Sneddon, L. G. and Voet, D., "Crystal and Molecular Structure of 2-(η -cyclopentadienyl)-2-cobalta-nido-pentaborane(9)", *Chem. Comm.* 118 (1976)

Epstein, R. H., Zeiger, A. V., Crocker, C. and Voet, D., "The X-Ray Structure of the Molecular Complex 8-Bromo-9-ethyladenine · 5-Allyl-5-isobutylbarbituric Acid", *Acta Cryst.* (in press)

Shieh, H. S. and Voet, D., "The X-Ray Structure of the Molecular Complex 8-Bromo-9-ethyladenine · Cyanuric Acid Monohydrate", *Acta Cryst.* (in press)

11. Anisotropic Intermolecular Interactions and Rotational Ordering in Hydrogen-containing Solids

D. White, Professor of Chemistry

Postdoctoral Fellow: J. Kohl

Research Assistant: M. Semack

Support: ERDA

Objective and Approach: To develop a basic understanding of excitations in solids where there is appreciable molecular motion even at low temperatures from which the macroscopic behavior, particularly as it relates to the hydrogen isotopes can be deduced. The focus is principally on the anisotropic interactions and thus rotational ordering, and the solids investigated, hydrogen, deuterium, hydrogen chloride are mainly quantum crystals where the dynamic effects which distort and modulate the anisotropic interactions are large.

The approach here is mainly pulsed N. M. R. and optical studies at low temperatures together with some macroscopic investigations such as specific heat and thermal conductivity. The results of these investigations could have some practical application in isotopic separations of hydrogen-containing compounds.

Progress: Three types of investigations are currently in progress, namely (i) spin-lattice relaxation measurements of ortho-para mixtures of solid deuterium in the rotationally ordered f. c. c. phase; (ii) heat capacity measurements of ortho-para solid D_2 mixtures in the ordered state; (iii) observation of the effects of phonon coupling on rotation-vibration line widths of HCl trapped in solid argon matrices.

In the case of the ortho-para mixtures of solid deuterium, the investigations in the 1 to 4° temperature range have revealed some quantitative information concerning the energy gap in the librational density of states for the rotationally ordered state of the solid. Both the spin-lattice relaxation and heat capacity measurements suggest a linear dependence of the gap with para concentration in solids containing 70-90% para- D_2 . This is consistent with theories (A. B. Harris, Phys. Rev. B-2, 3495 (1970)) for the solid which assume an orientational ordering resulting from the molecular electric quadrupole interactions, modified to some extent by static and dynamic effects. A new dynamic effect, namely the "resonance" ortho-para conversion in the solid,

modulating the electric quadrupolar interactions is now being studied at temperatures below 1 K.

For matrix isolated HCl molecules in solid argon we have developed a theory, based on a simple atom-atom potential, for the effect of coupling of the molecular rotations with the lattice motions of the rare gas atoms. These calculations are compared with some preliminary experiments of the changes in rotation-vibration line widths for HCl with temperature in the range 4 to 22 K. For the R(0) and P(1) features of the spectrum the calculated change in line width is greater than experimentally observed but this is to be expected since the linear chain approximation over-estimates the low frequency phonon density of states. The origin of the line widths is of some considerable importance in isotope separations in solids by selective laser excitation and both the experimental and theoretical work are being continued.

Publications:

Allavena, M., Chakroun, H. and White, D., "Effect of Phonon Coupling on Rotation-Vibration Line Widths of Matrix Isolated Diatomic Molecules", Molecular Spectroscopy of Dense Phases, p. 365, Elsevier Scientific Publishing Co., Amsterdam, The Netherlands (1975)

White, D., "Heat Capacity of Ortho-Para Mixtures of Solid Deuterium in the Ordered State", Chem. Phys. (in press)

D. CHEMICAL AND EXTRACTIVE METALLURGY

1. High Temperature Metallurgical Chemistry

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D. R. Gaskell, Associate Professor of Metallurgy and Materials Science

Postdoctoral Fellows: N. L. Dagaev
I. D. Sommerville

Research Assistants: M. Byrne
A. W. Cramb
A. E. Lindemanis
L. M. Ruch
D. R. Sain

Support: NSF/MRL
AISI
IREX
U. of Strathclyde
Navy
ARPA/LRSM

Objective and Approach: The objective of this research program is to further our understanding of the mechanisms and complex equilibria which are involved in extraction and refining processes. The particular emphasis at the moment is on the kinetics of gas-metal, slag-metal, and slag-gas reactions. The experimental approach in gas-metal reactions is one of determining the rate-laws for decarburization and oxidation of liquid metals, particularly by CO_2 , using electrochemical cell methods, continuous solute - replenishment steady-state weight loss techniques and C^{14} exchange at controlled oxygen pressure. Combination of these results with existing chemisorption studies and ancillary work on surface properties is then used to sort out the complex interplay of chemisorption of solutes and the kinetics of dissociation of gas species at a surface.

In the case of slag-metal reactions, the emphasis is on the use of chronopotentiometry as a tool for determining the ionic constitution of simple silicates when dilute solutes are added and the state of oxidation is controlled.

A detailed understanding of the factors which influence the rates and equilibria of metallurgical processes will lead, in the long term, to

better technological control and efficiency in energy requirements in the winning of metals for our use.

Progress: This has been a year of good progress in studies of gas-metal reactions and transport properties of silicate melts. Work has now been completed on the kinetics of the decarburization of liquid iron by CO_2 at high carbon concentration. For very high purity iron, the forward rate constant, in $\text{mole cm}^{-2} \text{ sec}^{-1} \text{ atm}^{-1}$, is given by the equation

$$\ln k_f = -11700/T - 0.43$$

The pre-exponential factor is very close to the collision frequency for gas molecules at the surface and, accordingly, it appears that it is the rate of chemisorption of CO_2 which controls the decarburization rate rather than the rate of dissociation of adsorbed CO_2 . The marked sensitivity of the rate to trace quantities of sulfur has been thoroughly investigated and it has been shown that the interference is remarkably closely described by an ideal site-fillage chemisorption isotherm for sulfur, which in turn closely describes the published data on the depression of the surface tension of iron by sulfur. The theoretical equations for this were developed last year and were briefly described in the previous report.

The marked effect of sulfur, at dilute concentration, on the rate of decarburization of liquid iron is shown in the attached figure. The curves represent the behavior for ideal, Langmuirian adsorption of the interfering solute.

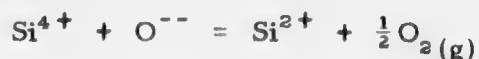
The existence of a significant residual dissociation rate on a fully covered surface has been demonstrated in the case of sulfur as the surface active solute but whether this is principally an artifact of the system, i. e., the rate of chemisorption of sulfur on the fresh surface limiting the coverage, is not yet clear.

Experimental progress has been made on developing a technique for the measurement of the rate of dissociation of CO_2 on those lower melting point metals which have substantial oxygen solubility. The metal is held in a high frequency induction furnace in an impinging gas jet configuration to take advantage of the high mass transfer characteristics of the RF stirring and the jet. It has been found possible to follow the oxygen concentration in the metal by means of a CaO-ZrO_2 solid electrolyte cell by carefully sheathing the interior of the cell by means of a thin nickel tube, thus avoiding significant RF pick-up.

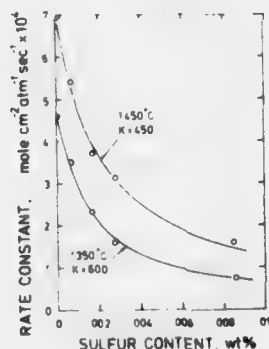
Studies of the transport and structural properties of molten silicates (slags) by high temperature chronopotentiometry have led to

techniques which give reproducible and precise chronopotentiograms at temperatures up to about 1200°C. Anodic transitions, tentatively ascribed to the O^{--} ion have been obtained at several compositions in the Na_2O-SiO_2 system but, more importantly, the sulfide ion has now been examined over a fairly wide range of composition and its approximate diffusivity has been determined. The addition of 2% F^- ion to the disilicate has been found to increase this apparent diffusivity by two orders of magnitude! These results are of practical significance in that fluorides are often used as fluxes in metallurgical processes - clearly more important phenomena occur than just the usually accepted melting point lowering.

Initial experiments on the sodium silicates at low oxygen potential have shown an apparent lowering of the O^{--} concentration, presumably by the equilibrium



Since this finding has important implications in slag-metal reactions at the low oxygen potentials typical of reducing reactions in metallurgical processes, this work is being extended to oxygen potentials at about the C-CO equilibrium.



Publications:

Choudary, U. V., Serkin, J. A. and Belton, G. R., "A Mass-Spectrometric Study of the Thermodynamics of the Fe-Cu and Fe-Cu-C_(sat) Systems at 1600°C", *Met. Trans.* **6B**, 399 (1975)

Belton, G. R., "Langmuir Adsorption, the Gibbs Adsorption Isotherm, and Interfacial Kinetics in Liquid Metal Systems", *Met. Trans.* **7B**, 35 (1976)

Sain, D. R. and Belton, G. R., "Interfacial Reaction Kinetics in the Decarburization of Liquid Iron by Carbon Dioxide", *Met. Trans.* **7B**, (in press)

2. The Nature of Complex Oxide Melts

D. R. Gaskell, Associate Professor of Metallurgy and Materials Science

Research Assistants: S. Ali
J. A. Burgo
B. K. D. P. Rao

Support: NSF/MRL
NSF
AISI

Objective and Approach: The objective of the project is a determination of the origins of the physicochemical behavior of complex oxide melts. Such systems are used as slag phases in pyrometallurgical slag-metal refining operations, electrolytes in molten salt electrolysis, fluxes in welding processes and occur as the coal slag in coal gasification and magnetohydrodynamic operations. The extents to which desirable properties can be exploited and undesirable properties can be eliminated or minimized are determined by the extent of understanding of the origins of these properties. The fundamental questions of interest are (i) what determines the rates at which slag-metal and slag-refractory reactions occur, (ii) to what extent do these reactions proceed before thermodynamic equilibrium is attained and (iii) what determines this equilibrium state? Answers to these questions are being sought through determination of the constitutions or atomic-scale structures of complex oxide melts. Two approaches are being made. The first involves determination of the ionic constitutions of binary and ternary silicate systems and the second involves determination of how the physicochemical properties of these systems are influenced by the presence of small quantities of added solutes.

Progress:

Cryoscopic Studies in Fluoride-Oxide-Silica Systems (Completed)

The depressions of the freezing temperatures of NaF and KF by additions of $3M_2O \cdot 2SiO_2$, $M_2O \cdot SiO_2$, $M_2O \cdot 2SiO_2$ and SiO_2 (where $M = Li, Na$ and K), the depressions of the freezing temperatures of MgF_2 , CaF_2 and BaF_2 by adding $2MO \cdot SiO_2$, $3MO \cdot 2SiO_2$, $MO \cdot SiO_2$, $2MO \cdot 3SiO_2$ and $MO \cdot 2SiO_2$ (where $M = Mg, Ca$ and Ba) and the depressions of the freezing temperature of PbF_2 resulting from additions of $2PbO \cdot SiO_2$, $3PbO \cdot 2SiO_2$ and $PbO \cdot SiO_2$ have been measured. The variations of the activities of the fluorides with liquidus composition have been calculated and these are shown to be in good agreement with proposed theoretical

models of the constitutions of these melts. In alkaline systems of $M_2O/SiO_2 > 1$ and in alkaline earth systems of $MO/SiO_2 > 1.5$ linear chain silicate ions and free F^- ions are postulated, and in alkali systems of $M_2O/SiO_2 < 1$ and in alkaline earth systems of $MO/SiO_2 < 1.5$ reaction between F^- and silicate ions to produce polyfluorosilicate anions is postulated. In the lead fluoride-silicate systems fluorination occurs at $PbO/SiO_2 = 2$, and in contrast with the alkali and alkaline earth systems, it appears that polyfluorosilicate anions and free O^{2-} ions can coexist in lead fluorosilicate melts. The deduced dependence of solution mechanism of fluorides in silicates on metal oxide/silica ratio is in agreement with conclusions drawn from infra red absorption studies of $NaF-Na_2O-SiO_2$ and $CaF_2-CaO-SiO_2$ glasses and provides a partial explanation of the dependence, on slag composition, of the effect of fluorides on the viscosities of silicate slags.

Thermodynamics and Theory of the Structure of Binary Silicate Melts (Completed)

Application of the principles of classical polymer theory to binary systems has facilitated calculation of the most probable size distributions of polysilicate anions in these systems. Two models are reported in the literature; one in which only linear chain silicate anions form and another in which branching chain silicate ions can form. On the assumption of ideal ionic mixing, it is found that the thermodynamic properties of linear chain systems differ from those of branching chain systems. Application of Guggenheim's statistical thermodynamics of polymer systems has permitted calculation of the free energies of mixing and the activities of solution components independent of the assumption of ideal ionic mixing. This has shown that the thermodynamics of mixing in polymerized silicates are independent of whether linear or branching chains occur, and, in comparison with experimental results, has quantified the extent to which chain polymerization theory can be applied to real silicate systems. It is now obvious that, within the composition range of interest, the formation of cyclic silicate ions is significant - a situation which, as yet, cannot be dealt with by the statistical methods of classical polymer theory.

The Free Energy of Formation of Melts in the System $Mn_2SiO_4-Fe_2SiO_4$ (Continuing)

The equilibration of Fe-Mn foils with melts in the system $Mn_2SiO_4-Fe_2SiO_4$ permits the determination of the solution properties of the latter system. This project follows examination of the mixing properties of $Co_2SiO_4-Fe_2SiO_4$ melts and is part of an on-going investigation of the thermodynamic properties of ternary silicate melts.

The Thermodynamics of Mixing in $\text{MnO-B}_2\text{O}_3\text{-SiO}_2$ Melts (Continuing)

This project is concerned with studying the properties of melts containing two acidic oxides and one basic oxide.

Mass-Spectrometric Studies of the Thermodynamic Properties of Complex Silicate Melts (Continuing)

Mass-spectrometric analysis of the equilibrium vapors effusing from a Knudsen cell permits the study of the thermodynamic properties of a range of systems which are not amenable to activity measurement by conventional methods. Ternary systems of interest to non-ferrous extraction processes are being studied in this project.

The Fluxing Properties of B_2O_3 in Steelmaking Slags (Continuing)

In an attempt to provide a quantitative comparison between CaF_2 and B_2O_3 as steelmaking slag conditioners, this project involves measurement of the solubility of Ca_2SiO_4 in ternary systems $\text{FeO-CaO-SiO}_2\text{-CaF}_2$ and $\text{FeO-CaO-SiO}_2\text{-B}_2\text{O}_3$.

The Activity of P_2O_5 in Steelmaking Slags (Continuing)

Through measurement of the phosphorus and oxygen contents of liquid iron equilibrated with CaO -saturated steelmaking slags, the activity of P_2O_5 in these slags is being determined. It is planned to study the influence of various slag conditioners, e.g., CaF_2 , B_2O_3 and TiO_2 on the activity of P_2O_5 .

Publications:

Gaskell, D. R., "Metallurgy", Encyclopaedia Britannica Yearbook (1975) p. 325

Gaskell, D. R., "Activities and Free Energies of Mixing in Binary Silicate Melts", Metal. Trans. (Accepted)

3. The Chemical Behavior of High Temperature Species

L. G. Sneddon, Assistant Professor of Chemistry

Postdoctoral Fellow: L. Hall

Research Assistant: J. S. Plotkin

Support: NSF/MRL
RC
KCC

Objective and Approach: Over the past 30 years, a great deal of research has been conducted on the production and characterization of high temperature species formed by the evaporation of the solid elements and compounds. The species are, in general, extremely reactive and undergo chemical reactions not characteristic of the elements in the condensed phase at lower temperature. Only recently have high temperature vapor species been used in synthesis, but preliminary results indicate that high temperature methods may be the synthetic and extractive methods of the future.

The basic technique consists of co-condensing the reactive high temperature vapor species with an appropriate ligand at a low temperature. The technique has the advantage that while the metal is a reactive high temperature species, the reaction with the ligand actually occurs at a very low temperature, thereby producing compounds which could not be produced in more conventional ways.

Besides its potential as a synthetic method, the technique also allows a unique way to study the reactivities of materials at high temperatures. Conventional high temperature studies have usually involved the reaction at a surface only. This new technique allows the formation and study of discrete compounds and should allow a determination of not only the final end product of a reaction, but should allow a trapping of intermediates produced.

The objective of the proposed research is to study the reactivities of high temperature species with a view to developing new synthetic and extractive processes.

Progress: Within the last year the construction of a high temperature vaporization apparatus and an accompanying vacuum system was completed. Since that time we have studied the reactions of a wide variety of high temperature metal vapors, including: copper, indium, nickel,

chromium and tungsten. Initial projects have emphasized the use of metal vapor species as reagents for inorganic and organometallic synthesis.

For example:

1. We have obtained preliminary results indicating that the compound $(C_2B_5H_7)_2Ni$ is formed from the reaction of nickel atoms and the small carborane, $C_2B_5H_7$, and we are currently investigating similar reactions with other metals.

2. We have used copper vapor as a reagent for several inorganic coupling reactions. For example, the reaction of divinylchloroborane with copper atoms has resulted in the production of the previously unknown, tetravinylidiboron.

The reactions of other atomic species have also been investigated. In particular, we have been interested in the reactions of sulfur atoms produced by the photolysis of sulfur-containing gases. Gunning and Strausz have shown that sulfur may be obtained as either singlet sulfur atoms (1D) or in the ground state (3P) by photolysis of carbonyl sulfide or carbon disulfide, respectively. These atomic species undergo a variety of insertion and addition reactions with parafins and olefins. We have found atomic sulfur species to be very reactive with inorganic compounds as well. We have produced the previously unknown compounds $C_2B_4H_6S$ and $C_2B_3H_5S$ by the reaction of sulfur atoms (1D) with $C_2B_4H_6$ and $C_2B_3H_5$, respectively. We feel this technique may be an important new method for producing sulfur-containing materials, and we are expanding our research in this area.

Publications:

Sneddon, L. G. and Voet, D., "Crystal and Molecular Structure of 2-(η -cyclopentadienyl)-2-cobalta-nido-pentaborane(9)", Chem. Comm. 118 (1976)

Plotkin, J. S. and Sneddon, L. G., "Photochemical Synthesis of Coupled Carboranes and Boranes", Chem. Comm. 95 (1976)

4. Chemical Behavior of Materials at Elevated Temperatures

W. L. Worrell, Professor of Metallurgy and Materials Science

Postdoctoral Fellows: S. Basu
T. Sasa

Research Fellows: M. F. Brady
S-K. Lau
K. L. Luthra
A. S. Nagelberg

Support: NSF/MRL
ARPA
NSF
AFOSR
ARPA/LRSM

Objective and Approach: An understanding of the corrosion of metals and alloys in complex gaseous environments is necessary to improve the operation and efficiency of many high-temperature processes, i. e., gas turbines, coal gasification. Kinetic studies of the corrosion of nickel and nickel-chromium alloys in mixed sulfur-oxygen atmospheres are being continued. The objective is to determine basic corrosion mechanisms, and the influence of alloy composition, temperature, and pressure on reaction rates and mechanisms.

Exceptionally stable platinum-transition metal compounds have attractive possibilities as protective coatings on transition metals used in corrosive environments. To provide the fundamental information necessary to assess their usefulness, the coherence and kinetic properties of these compound coatings are being determined. Platinum compounds are also important reaction products when platinum is used with refractory oxides in reducing atmospheres at high temperatures. Kinetic investigations of several platinum oxide reactions are being performed to determine their rate and mechanism as a function of temperature and oxygen pressure.

One major impediment to the development of new alkali-metal battery systems is the lack of suitable solid electrode materials. Transition-metal dichalcogenides intercalated with alkali metals offer exciting possibilities as reversible cathodes. However, the compositional variation of the chemical potential and diffusivity of the alkali metal in these intercalated compounds must be known. Electrochemical cell techniques are being used to obtain the thermodynamic and kinetic data which are necessary to quantitatively evaluate potential applications.

Progress: The simultaneous oxidation-sulfidation of high purity (99.999%) nickel in SO_2 - O_2 - SO_3 atmospheres at 600°C has been measured. Although thermodynamic equilibrium calculations predict the formation of a uniform NiSO_4 product layer, complex product layers of Ni_3S_2 and NiO are observed. The outer product layer is a NiO matrix containing thin channels or stringers of Ni_3S_2 . At 600°C the diffusivity of nickel (D_{Ni}) in Ni_3S_2 is $1.5 \times 10^{-7} \text{ cm}^2/\text{sec}$, while D_{Ni} in NiO is $1.8 \times 10^{-15} \text{ cm}^2/\text{sec}$. Thus, the Ni_3S_2 channels are regions of extremely rapid transport of nickel through the product layer. Even if the cross-sectional area of Ni_3S_2 is only 0.1% of the product layer area, the corrosion rate will be 10^5 higher than that for pure oxidation. Assuming that all nickel transported across the outer product layer is through Ni_3S_2 channels, values for D_{Ni} in Ni_3S_2 have been calculated from our measured corrosion rates. The calculated values are in good agreement with the literature values. These results provide the first quantitative picture of the reaction mechanism for such a complex gas-solid corrosion reaction.

Coherent intermetallic compound layers have been formed on titanium, zirconium, niobium, and tantalum by annealing platinum-coated foils at temperatures between 600 and 1200°C . Formation rates of the platinum intermetallic layers, as determined by layer-thickness measurements, follow the parabolic rate law. A layer-growth model has been developed to quantitatively analyze diffusional processes in multiple intermetallic layers. Using this model and layer-thickness measurements, values for the interdiffusion coefficient in each intermetallic layer at 800°C have been calculated.

Platinum disks have been reacted with ZrO_2 , Ta_2O_5 and Al_2O_3 powders at 1400°C under three different oxygen pressures (10^{-9} , 10^{-12} , and 10^{-18} atm) established by $\text{H}_2/\text{H}_2\text{O}$ gas mixtures. As expected, the reaction rate increases with decreasing oxygen pressure. Reaction products on the platinum disks have been characterized using X-ray diffraction, optical microscopy, and the electron microprobe. Besides an MPt_3 product layer, electron microprobe examinations indicate extensive dissolution of zirconium and tantalum into the platinum. Weight gains of the platinum disks follow a parabolic variation with time, which indicates that solid-state diffusional processes control the platinum-oxide reaction rates.

New solid alkali-metal electrodes have been prepared by intercalating 2H-TaS_2 with lithium and sodium. Intercalation is achieved using organic solutions containing the appropriate alkali ion. Unusually high open-circuit voltages have been obtained from cell (A) in which the anode is pure A (Li or Na) and the cathode is $\text{A}_{0.8}\text{TaS}_2$.



For example, a lithium cell has a value of 1.7 volts at room temperature and a sodium cell has a value of 1.0 volt at 200°C. These initial results are extremely exciting because cathodes having lower concentrations of lithium or sodium will yield even higher values.

Publications:

Meschter, P. J. and Worrell, W. L., "An Investigation of High-Temperature Thermodynamic Properties in the Pt-Ti System", *Met. Trans.* 7A, 299 (1976)

Francis, R. W. and Worrell, W. L., "High-Temperature Electrical Conductivity of Aluminum Nitride", *J. Electrochem. Soc.* 123, 430 (1976)

Worrell, W. L., "Overvoltage Phenomena in Solid-Oxide Electrolyte Cells at Elevated Temperatures", in Electrocatalysis on Non-Metallic Surfaces, Proc. of a Workshop held at NBS, Gaithersburg, Maryland, December 9-12, 1975

Worrell, W. L. and Nagelberg, A. S., "Structural, Thermodynamic, and Kinetic Properties of Electrode Materials", Proc. of Symposium and Workshop on Advanced Battery Research and Design, Argonne National Laboratory, March 22-24 (1976)

Worrell, W. L., "Oxide Solid Electrolytes", Chap. in Solid Electrolytes, Ed., S. Geller, Vol. in Topics in Applied Physics, Springer-Verlag KG, Berlin-Heidelberg

E. ELECTRONIC AND MAGNETIC MATERIALS

1. Magnetic Materials

H. B. Callen, Professor of Physics

Support: NSF
 ONR

Objective and Approach:

A. Growth-Induced Anisotropy in Garnets ("Bubble" Materials)

The understanding of growth-induced anisotropy in garnets remains a fundamental problem underlying the development of magnetic bubble memories. We are continuing our work in this field, both for practical reasons, and also because the phenomenon is a unique key to the understanding of fundamental aspects of surfaces and of crystal growth. The growth-induced anisotropy is established at the instant of crystallization and it reflects the surface properties which control the condensation of ions onto the surface. It is the only bulk property which retains vestiges of growth dynamics and which permits a study of surface properties using volume techniques.

The primary mechanism of growth-induced anisotropy in mixed rare-earth garnets is reasonably well understood in general terms. A secondary mechanism, involving dia-magnetic rare earth ions, has been observed, and again the general theoretical framework has been given. However, the keyword in both of these statements is "general". Essentially we have given only the structure of a theory, but the parameters of the theory are totally unevaluated. Thus, we assign different "site-preferences" to different ions, but the values of the "site-preferences" for each type of ion are undetermined. The virtue of such an initial approach is obvious; it has demonstrated that the postulated mechanisms are capable in principle of accounting for observed phenomena, and it has provided an algorithm for the interpretation of experimental data (in terms of empirical site-preference parameters). It is necessary now to subject the site-preference parameters to more penetrating theoretical analysis.

B. The Orientational State of Solid Hydrogen

One can prepare solid H_2 having a concentration x of $J = 1$ (ortho) and $1-x$ of $J = 0$ (para) molecules. The $J = 0$ molecules are spherical

whereas the $J = 1$ molecules have 3 possible orientational states and are thus essentially spin 1 systems. As the temperature is lowered the $J = 1$ molecules become ordered in a way that is closely analogous to the ordering of a magnetic system. The ordered phase is one in which the molecules may be divided into four sublattices. Each of the four sublattices has all its molecules oriented along one of the four different (111) directions.

a) Librons in Concentrated $J = 1$ Solids

The $J = 1$ molecules in the ordered state condense into a $J_z = 0$ state where the z axis lies along the classical equilibrium direction. The small oscillations of the $J = 1$ molecules into the $J_z = \pm 1$ excited states are called librons. Librons in solid H_2 (or D_2) are very similar to spin waves in an antiferromagnet. We are studying the librons as a function of x motivated by the following reasons. Firstly, there has been considerable interest in the analogous problem of spin waves in magnetic alloys and we have reported progress in this direction. Solid D_2 and H_2 are very favorable systems in which to study the effect of dilution on elementary excitations. Here the non-rotating $J = 0$ molecule with regard to its center-of-mass properties is essentially identical to the $J = 1$ molecules. So an alloy of $J = 1$ and $J = 0$ molecules represents an alloy in which the two components differ only in angular momentum. Secondly, since anharmonic effects are important in the pure system these alloys may provide a unique opportunity to study the combined effects of disorder and anharmonicity within a well defined context. Thirdly, it is in solid D_2 that one has very good experimental data as a function of x .

b) Magnetic Phases of Europium Chalcogenides

Europium selenide and the binary solutions EuS_xSe_{1-x} and $EuTe_xSe_{1-x}$ show complex spin structures and permit a detailed study of magnetic phase transitions, of the mechanism of direct and indirect exchange interactions, and of the interplay of these phenomena. The series EuO , EuS , $EuSe$ and $EuTe$, and the interpolated mixtures mentioned above, have simple nearest-neighbor and next-nearest-neighbor exchange, and both exchange constants vary smoothly across the series. Thus one has a rich, controllable, and conceptually simple series, and it exhibits a correspondingly rich range of phases and other properties.

Study of this system is of great theoretical interest for several reasons. The system is perhaps the "cleanest" example of a simple, but non-trivial Heisenberg model. The materials are also magnetic semiconductors, and a great deal of attention has been devoted to the interaction between the semiconductivity and the magnetic properties.

At or near EuSe the first and second neighbor exchange interactions cancel, and simple theories such as molecular field theory fail dramatically; the properties of the systems then depend on more subtle correlations. Hence these systems provide uniquely challenging tests of various statistical mechanical theories of magnetism.

Extensive Mössbauer studies of the binary solutions $\text{EuS}_x\text{Se}_{1-x}$ and $\text{EuTe}_x\text{Se}_{1-x}$ have been carried out by N. Bykovetz, who works in close association with our group. Nuclear magnetic resonance measurements of spin structures have been carried out by Komaru, Hihara and Koi. Both Bykovetz and Komaru et al. find complex spin structures in the neighborhood of EuSe (where J_1 and J_2 are approximately equal and of opposite sign) whereas the spin structures elsewhere are simple. These latter spin structures agree well with calculations which we gave some years ago, in collaboration with R. Tahir-Kheli and H. Jarrett.

Both simple molecular field theory and the random-phase approximation concord with the experimental results which suggest a "quasi-two-dimensional" structure. However, it can be expected that fluctuations will couple the planes weakly, and the role of these magnetic fluctuations is one area we intend to study further.

Another aspect of the fluctuation problem can be approached through the impurity problem. An impurity inserted into the system (at $J_2/J_1 = -1$ for the host) plays a very different role than an impurity in a true two-dimensional system, for it destroys the cancellation of the inter-plane couplings. Thus the impurity is a model of the magnetic fluctuation in coupling planes. We have studied impurity problems in magnetic systems, and we intend to extend these methods to the EuSe problem.

Progress: We have shown that the complex spin structures observed in EuSe by T. Komaru, T. Hihara and Y. Koi [J. Phys. Soc. Japan 31, 5, 1971] can be stabilized by the dipole interaction. Although the dipolar interaction is small relative to the exchange interactions, it can play a prominent role when the first and second neighbor exchange integrals closely cancel, as they do in EuSe. Our calculated phase diagrams place narrow limits on the J_2/J_1 ratio, which are inconsistent with current estimates.

2. Surface Waves in Optical Waveguide Structures

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Research Assistants: T-W. Hou
H. H. Verheggen

Support: NSF/MRL
NSF

Objective and Approach: The purpose of this project is to study experimentally and theoretically the characteristics of optical and elastic surface waves in optical waveguide structures. The high concentration of the optical field in the waveguide offers a means to excite elastic surface waves via electrostriction. This scheme involves two optical guided waves, one of which has its frequency shifted with respect to the other. Transduction of an acoustic surface wave at the difference frequency occurs through electrostrictive mixing. Different optical waveguide modes are being considered for the coupling. A pulsed ruby laser is used as the optical source. However, it is expected that cw operation is possible with commercially available cw lasers. The laser excited sound waves can be detected directly with interdigital transducers or by using the optical probing technique.

Progress: Glass optical waveguides are being fabricated by the E-gun deposition or by the silver ion diffusion techniques. We are setting up to fabricate metal diffused LiNbO_3 and LiTaO_3 waveguides. An integrated optics Laboratory is set up. A pulsed ruby laser has been fixed. Optical waveguiding effect has been observed with the ruby laser. Glass prisms are used as the couplers. A water-cell acousto-optic modulator has been constructed to split and frequency-shift the laser beam at 30 and 90 MHz. A preliminary experiment on the electrostrictive mixing did not yield the desired result, indicating critical laser beam alignment requirements.

The coupling equations are derived theoretically. The transverse field distributions of the optical and acoustic waves are included in the derivation. Different optical mode coupling schemes are being considered.

Publications:

Chang, M. S., Chang, W. S. C., Sopori, B. L., Vann, H. R., Muller, M. W., Craford, M. G., Finn, D., Groves, W. O. and Herzog, A. H., "GaAs Optical Waveguide Structures at $10.6 \mu\text{m}$ Wavelength", *Applied Optics* 14, 1572 (1975)

Share, S. , Epstein, A. S. , Monse, T. , Chang, W. S. C. and Chang, M. S. , "Radiation-Induced Effects in GaAs Thin-Film Optical (10.6 μm) Waveguides", Appl. Phys. Lett. 28, 340 (1976)

Chang, M. S. , "Acousto-Optic Filters", IEEE Circuits and Systems 10, April (1976)

3. Magnetic Properties of Disordered Materials

T. Egami, Assistant Professor of Metallurgy and Materials Science

Postdoctoral Fellow: T. Ichikawa

Research Assistants: J. T. Prater
R. S. Williams

Support: NSF/MRL
U of P
NSF
ARO-D

Objective and Approach: Amorphous magnetic materials and compositionally disordered crystalline magnetic materials are of interest both scientifically and technologically. They exhibit properties quite distinct from perfect crystalline magnets reflecting the degree of disorder, and some of these properties are technologically useful. In particular, transition metal based ferromagnetic amorphous alloys have excellent soft magnetic properties, and could be directly used for transformers and motors. Since the discovery of these materials was rather recent, there are a number of unresolved problems and ample possibilities of development. We continue our effort in this area, particularly focusing on: 1) effects of annealing on magnetic properties and structure relaxation, using the energy dispersive x-ray diffraction; and 2) compound effects of annealing and deformation by rolling and by creep on microstructure (internal stress distribution, crystallinity) and viscosity of amorphous alloys.

At the same time, in order to obtain more fundamental knowledge of the effect of disorder on magnetic properties, we will study the temperature and field dependence of magnetization in randomly diluted crystalline magnets: 1) $\text{RbMn}_{1-x}(\text{Zn}, \text{Mg})_x\text{Cl}_3$ - dilute paired antiferromagnet which is expected to show higher critical concentration than the percolation limit; 2) various dilute iron garnets - of which magnetic parameters are well known.

Also, as part of the group effort on temper embrittlement of alloys (C. J. McMahon et al.), Auger spectroscopy study of amorphous alloys and the direct study of cohesion of crystalline and amorphous transition metal-metalloid system will be carried out.

Progress:

Amorphous Magnetism

a) Accomplishments:

1) The origin of the magnetic anisotropy in transition metal base amorphous magnetic alloys has been a mystery, and active discussions have been made. We lead the field, along with Luborsky of G. E., to show that the internal stress is the origin of the anisotropy in the as-quenched material, and in the field annealed material the atomic pair ordering causes the anisotropy, by studying the temperature dependence of the anisotropy and the magnetoelastic effect.

2) We found that mechanical deformation by rolling of amorphous alloys drastically increases the magnetic anisotropy. This indirectly suggests that the dislocation-like defects can be created by deformation. The annealing is effective to reduce this anisotropy (due to the internal stress).

3) We found that the annealing of the amorphous alloy in the magnetic field perpendicular to the length of the ribbon is very effective in reducing the a. c. magnetic loss. When improved, the amorphous alloys have less a. c. loss (~ 20 milliwatt/lb. at 5 kG) than permalloys. It is suggested that the iron-base amorphous alloys might replace Si-iron in power transformers.

4) In the joint effort with C. D. Graham, the annealing behaviors of stress-relief, anisotropy and the fracture strength were studied, and it was shown that they have similar kinetics, suggesting common origins of the phenomena.

b) Continuing Efforts:

1) The unit of energy dispersive x-ray diffractometry was built in the machine shop, and the accessories are now being attached to the unit. Earlier, using the temporary model, it has been shown that the energy dispersive method indeed accurately provides the structure factor up to 20 \AA^{-1} , significantly beyond the current resolution limit. We are trying to determine the structure of amorphous alloys using this method, in particular, the effect of annealing and deformation.

2) A new method of measurement of high field magnetization, using a double-drive magnetometer, was developed. The method allows an accurate measurement of differential susceptibility at fields up to

135 kOe, and is particularly suited to study disordered magnets. RbMnCl_3 and garnet crystals will be studied using this method.

Magnetic Anisotropy of Crystalline Solids

Utilizing the high field facilities of LRSM, the field dependent magnetocrystalline anisotropy and magnetic moment of various solids (rare earth-iron-garnet, rare earth-aluminum-garnet, dysprosium) were studied at low temperatures. The main achievements were

- 1) The power law of the field induced anisotropy $K(H) \sim m(H)^n$ predicted by Callen and Callen was confirmed for the first time, using $\text{Ho}_3\text{Al}_5\text{O}_{12}$ and $\text{Ho}_3\text{Fe}_5\text{O}_{12}$.
- 2) The origin of the growth induced magnetic anisotropy of Pr-Y-iron-garnet (one of the bubble device materials) was suggested to be the crystal-field.
- 3) Anomalous field dependence of the anisotropy of Pr-ion-garnet was discovered.
- 4) The negative field dependence of the 12-fold anisotropy in Dy predicted earlier (Egami and Brooks) was confirmed experimentally.

Miscellaneous

Gadolinium was found to intercalate in graphite. The product was not magnetic at 77 K.

Publications:

Egami, T., and Brooks, M. S. S., "Theory of Collective Excitation in Strong Crystal Fields. I. Dynamics of the Angular Momentum Tensor Operators", Phys. Rev. B12, 1021 (1975)

Egami, T. and Brooks, M. S. S., "Theory of Collective Excitation in Strong Crystal Fields. II. Application to S=1 Singlet Ground State Ferromagnet", Phys. Rev. B12, 1029 (1975)

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"Annealing Effects in Amorphous Magnetic Alloys", AIP Conf. Proc.
29, 218 (1976)

4. Semiconductors: Defects and Disorder

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S. Rabii, Associate Professor of Electrical Engineering and Science

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Support: NSF/MRL

Objective and Approach: Many of the electronic devices employed today are constructed from materials whose properties are controlled by atomic-size defects and impurities (i. e., vacancies, interstitials, dopant atoms), gross topological disorder (glassy or amorphous semiconductors and insulators) or compositional disorder (random substitutional alloys). The long-term goal of this program is to provide a detailed picture of the electronic states in these kinds of materials, using a variety of spectroscopic and modulation techniques.

Of immediate current interest is the nonlinear variation in bandgap with alloy fraction which is generally observed in solid solutions such as $\text{GaAs}_{1-x}\text{P}_x$. Design of materials with given bandgap requires an understanding of the disorder phenomena which give rise to the observed nonlinearity. The semiempirical quantum dielectric theory of Van Vechten has been highly successful in treating these effects in simple pseudobinary alloys, wherein two different atoms of identical valence are randomly placed on one sublattice. The immediate goal of this work is to extend the theory to include nonisoelectronic alloys, several of which are of immediate importance in technology: the infrared laser material $\text{Pb}_{1-x}\text{Cd}_x\text{S}$, and the potential solar cell base material $(\text{CuInSe}_2)(2\text{ZnSe})$.

Progress: In binary semiconductor alloys of the form $\text{A}_x\text{B}_{1-x}\text{C}$, one usually finds a quadratic dependence of interband critical point energies on alloy fraction:

$$E(x) = E(0) + bx + cx^2.$$

The "bowing parameter" c is determined by the compositional disorder associated with random occupancy of A and B atoms on a perfect sublattice; in the rigid band approximation $c = 0$. Two major approaches are employed to understand c . The Coherent Potential Approximation is a detailed theoretical framework which, with major computational effort, provides excellent results even in small-gap systems such as $\text{Pb}_x\text{Sn}_{1-x}\text{Te}$, as found by Lasseter and Rabii. The quantum dielectric method of Van Vechten is a semiempirical approach which identifies the

short range fluctuation potential with the dielectrically-defined electro-negativity difference between A and B atoms:

$$C_{AB}^2 \sim \left(\frac{Z_A}{r_A} - \frac{Z_B}{r_B} \right) e^{-k_s R},$$

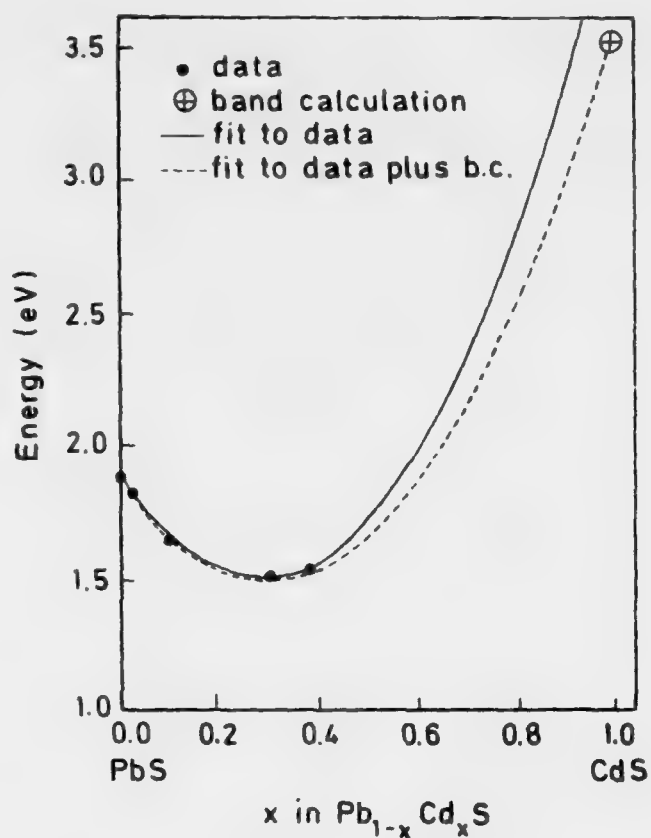
where Z and r are the valence and ionic radii, k_s is the Thomas-Fermi screening wave vector, and R is the average radius of a diatomic molecule in the solid. The bowing parameter is in turn given by

$$c = c_i + c_e = c_i + C_{AB}^2 / A$$

where c_i represents the long-range contribution which exists in the virtual crystal approximation, and c_e results from fluctuations on the order of a unit cell. The bandwidth parameter A is found empirically to be ~ 1 eV.

This theory has been found to work very well for III-V alloys with 8 valence electrons per diatomic molecule; it explains not only variations in bandgap, but also effective masses and spin-orbit splittings. In such systems $c_i \geq c_e$, since the substituting atoms come from the same column of the periodic table, hence $Z_A = Z_B$ and c_e is determined mainly by a size difference. Last year we studied $\text{Pb}_{1-x}\text{Cd}_x\text{S}$. The fact that here $Z_A - Z_B = 2$ leads to a theoretical c_e of 4.1 eV; c_i is expected to be < 1 eV. Our experimental value for the $E_g + \Delta_g$ gap is 4.8 eV, more than twice as large as any reported previously for isoelectronic substitutional alloys.

The dramatic nonlinearity introduced by the valence difference between Pb and Cd is shown in the figure below. The black dots are thermorefectance values of the $E_g + \Delta_g$ gap energy, obtained on vapor-deposited epitaxial films. The thin film technique allows us to make good crystals up to $x = 0.38$, whereas the equilibrium solid solubility of Cd in PbS is 0.05. The $x = 1$ endpoint is theoretical, since rocksalt-structure CdS exists only at high pressure.



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5. Graphite Intercalation Compounds

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Support: NSF/MRL
ONR
PSEF
NSF
ARO
AFML
MERADCOM, Ft. Belvoir
ARPA/LRSM

Objective and Approach: Today's power technology is materials-limited in the sense that the room-temperature properties of copper and aluminum represent a compromise among electrical conductivity, density, strength and price. For example, 10% of the electricity generated in the U.S. during 1975 was wasted as joule heat in transmission lines. Thus an obvious impact would be made if one could devise a material which provides a better overall compromise of the above properties at ambient temperature. Such a material would provide an alternative to superconducting technologies now under development for rotating machines and transmission lines.

Graphite intercalation compounds have been known for 40-odd years. Preliminary results obtained at LRSM last year suggest that one may find, within this large class of synthetic metals, a material which will in fact provide a better combination of properties than Cu or Al for electrical transmission.

The program has three ultimate objectives:

- a) to synthesize well characterized graphite intercalation compounds with room temperature conductivities comparable to or even greater than that of copper.
- b) to obtain a basic understanding of the effects of intercalation on the electronic structure of these compounds. This understanding will provide the basis for the design of new materials.
- c) to develop composite materials which will allow the practical realization of highly conducting intercalation compounds which are also strong and light weight.

The peculiar metastable properties of some members of this class suggest the following secondary goals:

- d) to understand the chemical reactions by which the compounds are formed, with a view toward assessing manufacturability.
- e) to explore their suitability as vehicles for heavy metal catalysts.
- f) to assess the possibility of employing them as solid electrolytes.

Progress: Milestones achieved to date fall roughly into three categories: conceptual, experimental and practical.

A. In trying to understand differences between donor and acceptor compounds we have gained new basic insights into how the conductivity is increased by intercalation. The most striking physical change induced in graphite by intercalation is an increase in a-axis conductivity σ_a by as much as a factor of 50 depending on intercalant specie and concentration. As the concentration increases from zero, σ_a increases more rapidly if the intercalant is an electron acceptor (halogen, acid) than if it is a donor (alkali metal). The different initial rates can be explained in part by the density of states in pure graphite, which we obtained analytically from the Slonczewski-Weiss-McClure Hamiltonian. Starting at E_{f0} , the Fermi energy in pure graphite, $N(E)$ increases more rapidly with decreasing $E < E_{f0}$ than with increasing $E > E_{f0}$. For equal total charge transfer, $N(E)$ on the acceptor side is about twice $N(E)$ for donors. This work was performed in cooperation with Prof. M. Dresselhaus of MIT.

The increase in σ_a is presumed due to an exchange of charge whereby some fraction of the valence electron or hole introduced by the

intercalant becomes a mobile carrier in the compound. If the intercalant is an alkali metal, one expects appreciable mixing between intercalant valence s and graphite $2p_z$ orbitals, in which case an important fraction of the valence electron is tied up in bonding (probably partially covalent) and thus unavailable for conduction. Similar mixing with acceptor valence orbitals (p -like or s - p hybrids) should be weaker and the conduction hole density potentially larger. The different valence mixing manifests itself in an increase in c -axis conductivity for donors but a decrease for acceptors, and in an apparent thickness of the intercalant layer less than an ionic diameter for donors, comparable to an ionic diameter for acceptors.

These simple analyses explain why acceptor compounds are the materials of choice, at least for the moment.

B. The experimental efforts to date have been concentrated in the areas of optical and transport studies. A major result was the observation of Drude edges in the reflectance spectra of the compounds of HNO_3 and SbF_6 . Comparison of $\sigma(\text{opt}) = \omega_p^2 \tau / 4\pi$ with $\sigma(\text{dc})$ for $\text{C}_{6n}\text{HNO}_3$ indicates that these compounds are not simple metals because $\sigma(\text{dc})$ always exceeds $\sigma(\text{opt})$ (by a factor of 40 for $n = 3$) and because $\sigma(\text{opt})$ increases with concentration for $n < 4$ whereas $\sigma(\text{dc})$ decreases slightly. The existence of well-defined plasma edges indicates a greatly increased interband threshold energy compared to pure graphite.

A computer controlled quantum oscillation apparatus has been constructed and tested by observing oscillatory magnetoresistance in pure graphite. This apparatus will be used to study the Fermi surface of the compounds. The same apparatus has already been used to measure the low field (non-oscillatory) magnetoresistance in nitric acid compounds. This experiment indicates that the carrier mobility is substantially reduced by intercalation.

C. Electrical conductivity measurements were made at room temperature on composite wires consisting of a copper sheath with an SbF_6 -graphite core. A mixture of 10μ graphite powder and sufficient SbF_6 to produce a stage 3 compound was sealed in a 6.4 mm O. D. copper tube and heated overnight at 150°C . The tubes containing the compound were cold swaged to an O. D. of 1 mm. A similar tube filled with pure Cu powder was the control. The composite conductivity was calculated from the measured resistance and the known geometry of the samples. Correcting for relative cross sectional areas of core and sheath, and considering the slightly less than ideal density of the core, the conductivity of the graphite intercalation compound was found to be $(8 \pm 1) \times 10^5 \Omega^{-1}\text{cm}^{-1}$ or almost 150% that of pure copper. This must be considered

a lower limit due to the possibility of interparticle impedances; the electron mean free path has yet to be determined. Bulk measurements on this interesting compound are currently frustrated by lack of contact integrity in the SbF_6 environment.

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6. a. Kinetics and Mechanisms of Graphite Intercalation
- b. Structure and Properties of Polymers

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Research Assistant: J. Hoffman

Support: NSF/MRL
NIH

Objective and Approach:

a. Other members of the Graphite Group within the LRSM have described the exciting physics to be done on graphite intercalation compounds, and told of their importance as materials of the future. It is equally true that virtually nothing has been published about the mechanism by which molecular species move into and out of the interlaminar regions of the graphite crystal. Indeed nobody has even reported what other products (if any) are formed during intercalation and de-intercalation. Not only is knowledge of intercalation chemistry (including kinetics) essential for the design of practical intercalation processes, it is a totally new, fascinating and unexplored type of chemistry. Aside from its obvious relation to the preparation and stability of graphite intercalation compounds, this new chemistry promises to be a rich source of reactions, some of which may be of great economic importance in the future.

b. On a weight basis, polymer-graphite composites are one of the strongest materials known. Much more must be learned about the structure of this class of composites, however, before they can be used with confidence in many applications. In this research, we have been studying linear viscoelastic behavior of uniaxial composites as a function of temperature, time in an H_2O atmosphere at $100^\circ C$, surface treatment of the fiber and fiber content as a means of characterizing fiber-polymer interactions.

Progress:

- a. Kinetics and Mechanisms of Graphite Intercalation

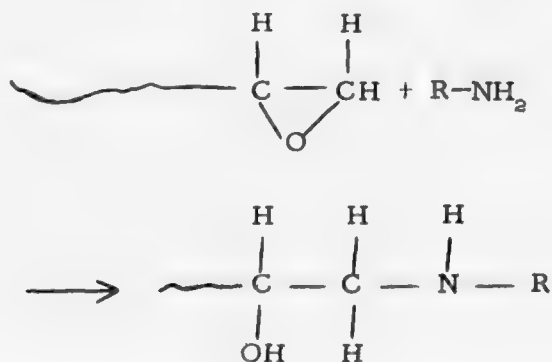
We have designed and have (nearly) finished construction of equipment for quantitative gas-phase intercalation. It consists of a vacuum rack fitted with appropriate glassware so we can do the following:

1. Evacuate a chamber containing the graphite, either as a crystal supported on the weighing pan of a quartz spring balance, or as a bed of finely divided material. We are adding the provision of conditioning the graphite, either by heating directly or with RF energy.
2. The vacuum will be broken by the intercalating atmosphere, and the reaction chamber maintained at controlled temperature and partial pressures of the various reactants.
3. With graphite crystals supported on the pan of a quartz spring balance, we can measure intercalation or de-intercalation as a function of time.
4. With the intercalating or de-intercalating atmosphere circulating through a bed of finely dried graphite, we can quantitatively determine reaction products by analysis of small samples of the gas phase by mass spectrometry or gas chromatography.

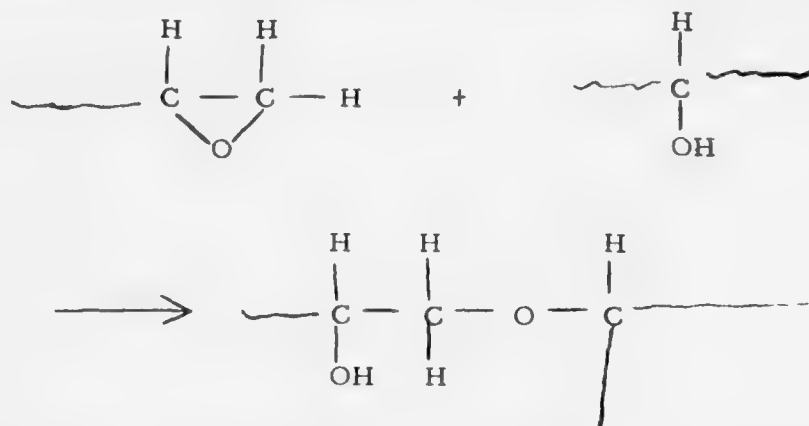
In addition, we completed a series of gas phase intercalations using HNO_3 . We found that the reaction is totally inhibited by the presence of oxygen and that NO_2 is formed during the intercalation reaction. Both of these observations are in agreement with the proposed intercalation mechanism: (1) adsorption of N_2O_5 (or adsorption of HNO_3 which reverts to H_2O and N_2O) at the surface of the graphite crystal, (2) $\text{N}_2\text{O}_5 \rightarrow \text{NO}_3^- \dots \text{NO}_2^+$, capture of an electron by NO_2^+ to give NO_2 which goes into the gas phase, (3) migration of NO_3^- into the graphite lattice, possibly accompanied by HNO_3 spacers.

b. Structure and Properties of Polymers

We have found that better heat resistant composites can be made using non-stoichiometric epoxide polymer matrices. The stoichiometric polymerization reaction is



With excess epoxy, we postulate the following secondary reactions also take place:



This secondary polymerization can be monitored by rubbery behavior above the glass transition and by the disappearance of an internal friction peak at 60°C. We postulate that it is this secondary polymer network that is responsible for the higher modulus at room temperature and the 20°C elevation of the glass transition.

Pu blications:

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7. Theoretical Study of Intercalated Graphite Compounds

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N. Holzwarth

Research Assistants: G. Luckman
R. Vishnov

Support: NSF/MRL
Juan March Fdn.
U of P

Objective and Approach: The purpose of this work is to develop a theoretical base for understanding the band structure and chemical binding in graphite lamellar compounds. In addition to the intrinsic interest of these highly anisotropic synthetic metals, they are important for possible use as light weight conductors in a variety of engineering applications.

The general approach is to use existing solid state theories of band structure and cohesive energy at two levels: a level of approximate models that can be applied to a wide variety of materials to discern chemical trends, and a level of greater detail in which fairly extensive calculations are performed on a single system (C_8Li). The approximate models are based on LCAO and Thomas-Fermi-Dirac-Kirzhnits methods.

Progress: Both the band structure work and the chemical binding work are in their initial stages. The LCAO model for examination of trends in compounds of the C_8M type has been set up and results should be forthcoming soon. The assumptions in this model are: 1. Only π -orbitals of graphite and valence orbitals of intercalant will be included in the basis set. 2. These orbitals will be taken to be those of pure graphite and the free atom respectively. 3. The crystal potential will be the sum of free atom potentials plus an electron-electron interaction based on Slater $X-\alpha$ exchange. 4. Only nearest neighbor interactions will be taken for the matrix elements and overlap integrals. 5. Three center integrals will be neglected.

The more detailed calculations for C_8Li are first being done by a KKR method at symmetry points in the Brillouin zone. The programming for this is nearly complete.

The first objective in the chemical binding work is to learn something about the distribution of electron density in the intercalated compounds. To this end, the degree of validity of a Thomas-Fermi-Dirac method, modified by the Kirzhnits correction to the kinetic energy, is being studied. We are doing this by performing TFDK calculations for metallic systems in which some information is available about the electron density. We have applied the TFDK method to a group of alloys of the β -brass type whose electron densities have been studied by an X- α self-consistent field calculation. The agreement for the charge transfer in these alloys between the two methods is satisfactory. Also, electron densities at the edge of the Wigner-Seitz cell as computed from the TFDK method agree reasonably well with those using APW wave functions. In short, we have demonstrated that the TFDK method gives reasonable results for electron densities outside ion cores. Inside ion cores, we use densities from free atom functions. We are now ready to apply the method to intercalated graphite compounds.

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Girifalco, L. A., "Criteria for Solid Solution Formation in NFE Alloys", Acta Met. (in press)

8. Structure and Properties of Magnetic Materials

C. D. Graham, Jr., Professor of Metallurgy and Materials Science

T. Egami, Assistant Professor of Metallurgy and Materials Science

Visiting Scientist: Y. Takei

Research Assistants: D. A. Doane
H. H. Liebermann
S. R. Trout

Support: NSF/MRL
Sony Corp.
NSF-RANN
NSF
ARO-D

Objective and Approach: The aim is to apply the methods of materials science to the study of magnetic properties, with particular emphasis on materials of actual or potential engineering importance. The work is deliberately extended to include both hard and soft magnetic materials (i. e., those hard and easy to demagnetize), since the same physical ideas govern the behavior of both classes. A central idea in most of the work is the importance of the domain wall behavior in determining magnetic properties, with consequent importance attached to the relation between domain wall arrangements and motion, and various kinds of structure. A serious effort is made to pick fundamental studies of direct relevance to understanding or improving real engineering materials, and to keep in communication with industries that make and use magnetic materials.

Progress:

Permanent magnet materials. High field measurements parallel and perpendicular to the alignment axis have been made at room temperature and below on a series of sintered SmCo_5 -type magnets of varying composition provided by the GE R & D Center. The results were used to determine the magnitude and temperature dependence of the effective magnetic anisotropy, and to disprove a claim in the literature that the coercive field depends directly on the bulk anisotropy. The data were also used to determine the degree of crystallographic alignment of the individual grains in the magnets. A simple statistical model of grain alignment was developed, and related to the principal experimental measurements of alignment, namely magnetic, x-ray, and metallographic.

Magnetoplastic deformation. Work has been completed on the plastic deformation of Dy single crystals subjected to high magnetic fields along the magnetic hard axis at 4.2 K. The deformation mechanism has been shown to be mechanical twinning, and a plausible explanation of the effect has been advanced. The difference in magnetostatic energy between the twinned and untwinned regions at fields on the order of 100 kOe translates to an equivalent stress sufficient to cause plastic deformation. Direct mechanical deformation of single crystals of Dy produces the same mode of deformation as the magnetic field.

Amorphous ferromagnetic alloys. Simple apparatus has been built for the production of amorphous alloy ribbons, thus freeing us from the whims of Allied Chemical in obtaining sample material. A number of new compositions have been made, and some magnetic measurements made. Working with Allied Chemical materials, the annealing behavior of amorphous ribbons has been studied. Relaxation of elastic stress at constant strain, changes in magnetic anisotropy, and changes in the fracture stress have been followed with time at constant temperature. The results have helped to confirm the conclusion that the ribbons as-prepared contain relatively large regions of highly non-uniform stress, and that this stress relaxes almost completely after annealing treatments that do not cause any measurable crystallization. The stress interacts with the (generally positive) magnetostriction to strongly influence the low-field magnetic properties. As the stress relaxes during annealing, the effective anisotropy decreases, with a resulting marked improvement in remanence and other magnetic properties. The origin of the brittleness that results from annealing most amorphous ribbons remains unclear. Our recent measurements show that annealing can increase the Curie temperature by substantial amounts (tens of degrees), but surprisingly the 0 K saturation is changed only slightly. We have learned how to prepare samples and orient them to see the domain structure in the scanning electron microscope, and expect this to be an important tool in further work. New amorphous alloy compositions containing B rather than P have been prepared, and show improved magnetic and mechanical properties.

MnBi Eutectics. A large amount of data has been accumulated on the magnetic behavior at high fields and temperatures from 77 to 300 K of MnBi-Bi eutectics. The magnetic behavior is complicated, not to say bizarre, and has not yet been successfully correlated with electron microscopy of the phases present. We struggle on.

Publications:

Graham, C. D., Jr., Egami, T., Williams, R. S. and Takei, Y., "Annealing Effects in Amorphous Magnetic Alloys", AIP Conf. Proc. 29, 218 (1976)

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9. Solid State Physics

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T. C. Lubensky, Associate Professor of Physics

H. B. Callen, Professor of Physics

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Research Assistants: J-H. J. Chen
C. Dasgupta
R. Fisch

Support: NSF/MRL
NSF
ONR

Objective and Approach: Random alloys, i. e., random mixtures of two or more components, give rise to the possibility of developing materials with an almost unlimited range of physical characteristics. The principles involved in predicting the material parameters of such systems are more complicated than those invoked for pure systems. It is reasonable to assert that the properties of an alloy of two materials A and B are intermediate between those of either pure material. It is essential, however, to replace this qualitative idea by a quantitative prescription for carrying out the averaging process involved. The approaches which we are using to deal with these problems involve either a) numerical techniques based on computer simulation, or b) analytic approximations. The value of using the two methods is that numerical approaches suggest improved analytic approximations which in turn lead to the development of more refined numerical techniques. Mainly we are concerned with mixed and amorphous magnetic systems although our techniques can be extended to treat phonons or electrons in mixed or amorphous crystals or to discuss the properties of glasses. Examples of the specific properties we try to calculate in these disordered systems are 1) spin wave energies, 2) domain wall stiffness, 3) perpendicular susceptibility, 4) magnetization as a function of temperature, and 5) critical behavior at the Curie temperature.

Progress:

1. We have calculated the response of a random antiferromagnetic alloy to an external magnetic field. Up to now, this problem has been treated by assuming that the atomic magnetic moments are deflected through a small angle by the external field. Now we have numerically solved the non linear problem which results when the small angle

approximation is not made. In this way we have reproduced the pronounced non linear dependence of magnetization on field experimentally observed by Breed et al.

2. We have analyzed the behavior of randomly diluted magnetic alloys when the concentration of magnetic ions is near the threshold, p_c , for critical behavior. For $p < p_c$ the magnetic ions form isolated islands whereas for $p > p_c$ one of the islands is infinitely large. We have defined exponents to describe the limiting behavior in various response functions such as the susceptibility for $p \rightarrow p_c$. We also have derived scaling relations between these exponents. We find that for spatial dimensionality, d , less than or equal to 2, an antiferromagnet is unstable in a small external field. Also we show that mean field theory is valid for $d \geq 6$.

3. We have discussed the "phase transition" which occurs at the threshold concentration p_c mentioned in paragraph 2 above. We have given the first complete formulation of this "phase transition". Previously a mean field theory for such purely geometrical quantities as mean square island size, mean perimeter of isolated islands, etc. was given by Toulouse. Mean field theory is valid for spatial dimensionality, $d \geq 6$. We have calculated corrections to mean field theory, using renormalization group techniques, in powers of $6-d$. We also gave the first complete numerical analysis of the data for $d = 2$. In this way we have shown how this "phase transition" relates to the usual ones.

4. We have analyzed the properties of magnetic spin glasses. These are magnets in which the orientations are locked into unpredictable metastable or stable equilibrium when the temperature, T_F is reduced below a "freezing" temperature, T_F . We have shown that $d = 6$ is the critical dimensionality in the sense that for $d \geq 6$ mean field theory is valid. Using renormalization group techniques we are able to calculate corrections to mean field theory in powers of $6-d$. Experiments ($d = 3$) show that the specific heat has a rather rounded cusp at $T = T_F$ and our results are consistent with this. Again, the advance we have made is to show that this critical freezing of a spin glass is related to the usual phase transition.

5. We have given the first quantitative estimate of the position dependence of the magnetization in a randomly dilute magnet. We have shown, by a Monte Carlo calculation, that the magnetization of an ion in such an alloy is directly related to the number of magnetic neighbors it has. While this conclusion is obvious, no effective way to calculate this effect had previously been proposed. Based on our numerics we propose simple analytic theories.

6. Mr. Dasgupta has related the desorption of adsorbed molecules (H_2) on a surface ($W, 100$) to the order - disorder problem. The desorption energy not only measures the bonding energy, but also includes crudely speaking the free energy due to adsorbate-adsorbate interactions. By a Bethe-Peierls approximation Mr. Dasgupta has shown that two different energies will appear in the desorption spectrum having amplitudes which are temperature dependent.

Publications:

Kirkpatrick, S. and Harris, A. B., "Theory of Spin Excitation of $Rb_2Mn_xNi_{1-x}F_4$ ", Phys. Rev. B 12, 4980 (1975)

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Dasgupta, C., "Renormalization Group Calculation of the Critical Exponents for Percolation" (Accepted)

10. Nonequilibrium Phenomena in Superconductors

D. N. Langenberg, Professor of Physics

Research Assistants: C. -C. Chi
S. B. Kaplan
T-w. Wong
J. T. C. Yeh

Support: NSF/MRL
NSF
ONR
U of P

Objective and Approach: The principal objective of this program is to understand the behavior of superconductors perturbed from the thermal equilibrium state. Nonequilibrium phenomena can be important in a variety of circumstances, e. g., in the transport of current across the interface between a normal metal and a superconductor, in the generation and detection of ultra-high-frequency phonons using superconductors, and in several types of superconducting weak link devices. The latter case is of particular interest because such devices are increasingly widely used in applications of the Josephson effects, while the fundamental mechanisms underlying their behavior remain poorly understood. We are investigating experimentally the superconducting nonequilibrium state in both thin films and in superconducting microbridges, using photon and current-injection excitation of quasiparticles. We are also studying theoretically the interactions between Cooper pairs, excited quasiparticles, and phonons in the nonequilibrium superconductor.

Progress: We have developed a new class of superconducting weak link devices, in which the weak region is created by locally driving the superconductor out of equilibrium using an independent source of quasiparticles. The quasiparticle source may be tunnel injection, injection through another weak link, or photon or phonon pair-breaking. The characteristics of these weak links can be controlled electrically or optically, hence the name we have given them, CLINK, for controllable link. We have successfully observed the ac Josephson effect in all types of CLINK. We have developed a theory which describes the spatial distribution of nonequilibrium quasiparticles in the CLINK, taking into account the injection geometry and quasiparticle diffusion and recombination. Using this together with existing theories which connect the nonequilibrium quasiparticle density with the depression of the superconducting order parameter, and theories of weak link behavior, we can

make predictions of various properties of the CLINK which are in reasonable accord with our experimental observations. We intend to continue our investigations of the various types of CLINKs, with the primary objective of answering various outstanding questions about the nonequilibrium superconducting state and the fundamental mechanisms of superconducting weak link behavior, but with an eye to possible practical applications of CLINKs in cryoelectronic systems.

We have shown experimentally that the quasiparticle current-voltage characteristic of a superconducting tunnel junction can be significantly affected by nonequilibrium effects due to self-injected quasiparticles. This effect has been previously observed but attributed to simple heating, an explanation we have been able to rule out experimentally. An analysis of our data yields a determination of the quasiparticle recombination time in tin in good agreement with the results of earlier experiments.

We have used our microwave-reflectivity technique to investigate quasiparticle recombination in photoexcited aluminum films. This work has led to a determination of the intrinsic recombination time in aluminum which is in excellent agreement with theory (see below) and which resolves discrepancies among other measurements.

In collaboration with F. Jaworski and W. H. Parker, University of California-Irvine, we have developed evidence that an inelastic phonon process invoked by Schuller and Gray to explain experimental results in the nonequilibrium state in superconducting films is probably spurious.

In collaboration with D. J. Scalapino, J. J. Chang, and S. Jafarey, University of California, Santa Barbara, we have completed a comprehensive theoretical study of quasiparticle and phonon lifetimes in superconductors. A formalism relating these times to the electron-phonon coupling function $\alpha^2(\Omega)F(\Omega)$ was used to calculate the quasiparticle inelastic scattering, recombination, and branch-mixing lifetimes, and the phonon pair-breaking and scattering lifetimes for about a dozen superconductors. The results provide a theoretical basis for comparison with a wide variety of experiments and resolve several puzzles in existing data.

We have developed from first principles a set of coupled kinetic equations for quasiparticles and phonons in superconductors and applied them to numerical computation of the distribution functions of quasiparticles and phonons in nonequilibrium superconductors. The purpose of this exercise was to check the validity of several popular but much over-simplified models currently used to describe nonequilibrium

phenomena. The results indicate that none of these models is really adequate but suggest which one to use if the more realistic but complete kinetic theory is impractical.

Publications:

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Langenberg, D. N., "Nonequilibrium Phenomena in Superconductors", in Low Temperature Physics - LT14, Eds., M. Krusius and M. Vuorio (North Holland/American Elsevier, Amsterdam/New York, 1975), Vol. 5, p. 223

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Buckner, S. A. and Langenberg, D. N., "Riedel Singularity in Tin-Tin Oxide-Tin Tunnel Junctions", J. Low Temp. Phys. 22, 569 (1976)

Jaworski, F., Parker, W. H. and Kaplan, S. B., "Quasiparticle and Phonon Lifetimes in Superconducting Pb Films", Phys. Rev. (Accepted)

Wong, T-w., Yeh, J. T. C. and Langenberg, D. N., "Controllable Superconducting Weak Links", IEEE Trans. in Magnetism (Accepted)

11. Cooperative Phenomena in Random Systems

T. C. Lubensky, Associate Professor of Physics

Research Assistant: J-H. J. Chen

Support: NSF/MRL
John Simon Guggenheim Fdn.

Objective and Approach: The objective of much of my research over the past has been to obtain an understanding of cooperative phenomena in random systems. The principal problems investigated were phase transitions in weakly diluted quenched magnets, cluster statistics near the percolation threshold in random lattices and spin glasses. Percolation and the spin-glass state occur only in strongly diluted or strongly random systems. The technique that has provided a truly powerful and unifying approach is the Wilson-Fisher renormalization group. This technique provides qualitative as well as quantitative results unobtainable by other methods.

Progress: The most outstanding accomplishments in the past year have been in the field of cooperative phenomena in random systems. This work was carried out in collaboration with A. B. Harris. We were the first to apply renormalization group techniques to cluster statistics near the percolation threshold. Consider a lattice in which bonds (or sites) can be present with probability p and absent with probability $q = 1-p$. For p less than a critical value p_c , there are only finite cluster. For $p > p_c$, an infinite connected cluster develops. The probability that a site is in the infinite cluster grows continuously from zero as $(p-p_c)^\beta$ for $p > p_c$, and is analogous to the order parameter in a phase transition. Similarly, the mean square cluster size diverges as $|p-p_c|^{-\gamma}$ near p_c and is analogous to the susceptibility. Other critical exponents can be defined in a similar way. Kasteleyn and Fortuin showed that the percolation problem could be described by the thermodynamics of the one state limit of a sequence of generalized s -state Potts models. Using this result, we were able to calculate critical exponents for the percolation problem using the ϵ -expansion, finite lattice renormalization groups and series expansion.

A spin glass is a magnetic state in which local magnetic moments are frozen in below a freezing temperature but in which there is no long range correlation in the direction of local ordering. Edwards and Anderson developed a model for this state in which the nearest exchange integral is a random variable with zero mean. Thus the system can be neither ferromagnetic nor anti-ferromagnetic. We developed a Landau-Ginzburg free energy for this model and calculated critical exponents

using the ϵ -expansion. Work on this model is continuing with emphasis on the competition between spin-glass and ferromagnetic ordering and on the effect of external magnetic fields.

Other work in the past year includes 1) an investigation of the effect that couplings of an order parameter to anisotropic elastic degrees of freedom has on magnetic and liquid crystal phase transition, 2) a continuing study of phase transitions in semi-infinite systems and 3) an analysis of models yielding nematic to smectic-C phase transitions in liquid crystals.

Publications:

Harris, A. B., Lubensky, T. C., Holcomb, W. K. and Dasgupta, C., "Renormalization Approach to Critical Phenomena", Phys. Rev. Lett. 35, 327 (1975)

Harris, A. B., Lubensky, T. C. and Chen, J. H., "Critical Properties of Spin Glasses", Phys. Rev. Lett. 36, 415 (1976)

de Moura, M., Lubensky, T. C., Imry, Y. and Aharony, A., "Coupling to Anisotropic Elastic Media: Magnetic and Liquid Crystal Phase Transitions", Phys. Rev. B13, 2176 (1976)

Priest, R. G. and Lubensky, T. C., "Two Tensor Models with Application to Percolation", Phys. Rev. B, (1976)

12. Spectroscopic and Chemical Properties of Small Aggregates of Binary Compounds and Metals

E. R. Nixon, Professor of Chemistry

Research Assistant: R. A. Teichman, III

Support: NSF/MRL
NSF

Objective and Approach: This research deals with several types of materials (particularly IV-VI compounds, sulfur nitride, and metals) which have potential utility as conductors, semiconductors or catalytic agents. The objective is to characterize the various spectroscopic properties of these materials as a function of the state of aggregation from the diatomic molecule (MX or M_2) to "dimers" of these species (M_2X_2 , M_4) and to larger aggregates or polymers (M_nX_n , M_n) so as to gain some understanding of how the polymers are formed. Then secondly, small molecules such as H_2 or CO will be brought into contact so as to react with these small clusters of atoms or molecules. The objective here is to provide some basic information on reactions at metal surfaces.

Progress: During the past year we have extended our studies of matrix-isolated species to some new systems, including diatomic and tetraatomic molecules of lead, bismuth, lead bismuth alloy, selenium and tellurium. In each case we have isolated the molecules for study as a dilute "solution" in a solid inert gas matrix at low temperatures. The main emphasis of the research has been to characterize the absorption spectra of the systems from the infrared through the ultraviolet and the emission spectra when the luminescence is excited by laser radiation, either with fixed frequency laser lines or tunable radiation from a dye laser. Because of the spectroscopic advantages and sensitivity of the technique, we have been able to characterize hitherto undiscovered electronic states of each of the species investigated. Even though our laser sources are limited to the visible and the very near ultraviolet portion of the spectrum, we have been able to observe biphotonic absorption by the species and subsequent emission in the far ultraviolet so that some high energy states of the molecules have become accessible.

New aspects of the interactions between the isolated molecules and the host matrix have been explored. By using a pulsed nitrogen laser as the source, we have now measured the radiative lifetime of a number of the electronic states of PbS , $PbSe$ and Pb_2 . The lifetimes, which thus far vary from a few microseconds to a few milliseconds, give indications as to the efficiency of various relaxation processes. By the use of tunable

continuous laser radiation we have been able to characterize the inhomogeneity of the environment of a PbS or Pb₂ molecule in a solid argon matrix, and to measure the degree of coupling between the vibronic states of such impurity molecules with the phonon states of the solid inert gas matrix.

The object of the careful characterization of the states of our species is to be able to study interactions then with foreign molecules. Experiments of a preliminary nature have been carried out in which O₂ molecules are allowed to interact with PbS and Pb₂S₂ molecules all within a matrix of solid argon. That interactions occur is evident from examination of the spectra of the separate matrix-isolated reactants and the interaction products but these differences have not yet been interpreted in terms of bond formation.

Work is continuing on the (SN)_x problem. We have been able to identify several components in the vapor of the sulfur nitride polymer (the primary component appears to be a radical S₄N₄ molecule). The nature of the study will be to carry out within a solid inert gas matrix the controlled, and therefore presumably understandable, polymerization of the species which exist in the vapors of solid S₂N₂, of the solid (SN)_x polymer, etc.

Publications:

Teichman, R. A., III and Nixon, E. R., "Absorption and Laser Excited Emission Spectra of Matrix-Isolated Pb₂", J. Molecular Spectroscopy 59, 299 (1976)

Teichman, R. A., III and Nixon, E. R., "Matrix Isolation Study of the Products of Volatilization of Polymeric Sulfur Nitride", Inorg. Chem. 15, 1993 (1976)

13. Theoretical Investigation of Electronic Properties of Solids

S. Rabii, Associate Professor of Electrical Engineering and Science

Research Assistants: S. W. W. Liu
C. Y-W. Yang

Support: NSF/MRL
ARPA
Max-Planck-Institut für Festkörperforschung
ARPA/LRSM

Objective and Approach: The objective of this work is to use, both long established and newly developed theoretical techniques for the study of electronic properties of certain solids with present and potential future applications. The work will include:

1. Continuation of the investigation of the electronic properties of nonisoelectronic pseudobinary alloys, specifically $\text{Pb}_{1-x}\text{Cd}_x\text{S}$. The approach will be a combination of the Coherent-Potential-Approximation Augmented-Plane-Wave method and model calculations.

2. Continuation of the study of the role of defects in the electrical and optical behavior of solids. The specific defects of interest will be vacancies, interstitial and substitutional impurities and the systems of interest range from NbO, amorphous Si, Pb chalcogenides, to semiconductor-oxide interface. The approach will be the study of clusters of atoms containing defects by the use of non-relativistic and full-relativistic Scattered-Wave-X α method.

3. Determination of the origin of a structural phase transformation that occurs in PbS at pressures $\sim 20\text{kb}$ and which reduces the symmetry of this material.

4. MgO is a material of interest for two reasons. First, it has potential applications as a catalyst and as a phosphore. Second, due to the fact that Mg is a smaller atom than Zn (ZnO is another potentially good catalyst), it serves as a simpler proving ground for the development of techniques for the study of surface effects in these materials.

We propose to apply the SCF scattered-Wave-X α technique to clusters of MgO containing a surface and also use band structure techniques to obtain the bulk properties. One specific aim is to investigate the polarizability of oxygen ions at the surface of MgC.

Progress:

1. We have developed the first fully relativistic Scattered-Wave- $X\alpha$ formalism and also developed the computer codes. The technique was applied to the study of the following problems:

- a) Electronic structure of molecules containing heavy atoms such as I_2 , H_2Te , PbS , $PbSe$, Pb_2S_2 , Pb_2Se_2 were calculated using this technique and the results are in good agreement with experiment.
- b) Electronic states associated with the occupation of vacancies by atomic H in PbS and $PbSe$ have been obtained and the role of atomic H in changing the electrical behaviour of these compounds have been confirmed in agreement with experiment.

2. Electronic energy bands and the density-of-states of the high pressure phase of CdS were calculated. The results are in excellent agreement with the available experimental data and have served to start new experimental effort in Germany and the Soviet Union to confirm the existence of a second forbidden gap in the conduction band of CdS under high-pressure which is predicted by our calculations.

3. We have calculated the electronic structure of Pb_4S_4 cluster as a function of the "lattice constant" and have shown that there exists a minimum in the total energy curve as a function of Pb-S separation. This is important in that it demonstrates that the muffin-tin potential is a good model for such a closed-packed cluster of atoms as Pb_4S_4 .

4. An extensive energy band calculation has been performed for MgO using the augmented-plane-wave technique and the $X\alpha$ exchange-correlation potential. The results are in excellent agreement with experiment, e. g., the calculated minimum band gap is 7.5 eV while the experimental gap is 7.7 eV. This is particularly significant since MgO had been singled out by other workers as a material requiring the full many-body treatment of correlation in order to be able to obtain reasonable results for the band gap. We have also carried out a scattered-wave- $X\alpha$ calculation for Mg_4O_4 cluster and the results agree well with both the calculated band structure and experimental data.

Publications:

Yang, C. Y. and Rabii, S., "Relativistic Scattered-Wave Theory", *Phys. Rev. A* 12, 362 (1975)

Liu, S. W. W. and Rabii, S., "Energy Band Structure and Density of States for CdS under High Pressure", Europhysics Conf. Abst. 1A, 39 (1975)

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Rabii, S., "Hydrogen Effect in Lead Selenide", Int. J. of Quantum Chem. (Accepted)

F. BIOMATERIALS

1. Biomaterials Research

S. R. Pollack, Professor of Metallurgy and Materials Science

E. Korostoff, Professor of Metallurgy and Materials Science

Research Assistants: J. B. Brunski
W. Iannacone
A. F. Moccia
A. Radovsky
R. J. Solar
W. Starkebaum
R. W. Treharne

Support: NSF
NIDR

Objective and Approach: The objective of this program is to determine the best method of replacing damaged, diseased or otherwise non-functioning parts of the human body. To accomplish this it is necessary to understand the fundamental properties of the tissues that are to be replaced, and to understand the properties of replacement materials that are used. This latter point requires an understanding of the effect of replacement materials on the body and the effect of the living environment on the properties of the material.

Progress:

Stress Generated Potentials in Bone

We have investigated the role of collagen in producing the observed electrical potentials in bone when external stresses are applied. A whole bone model was developed using excised femorae from Sprague Dawley rats, with a deformation mode in four point bending. It was observed that the electrical signal per unit strain increases with increased collagen cross linking and decreases with decreased cross linking. It was also shown that the magnitude of the electrical signal increases during maturation and the data strongly suggest that little or no electrical signal is present during the fetal stage.

We have developed a microelectrode system that enables the electrical signal to be measured as a function of position within an osteon during deformation. The results to date clearly indicate that the internal

field within an osteon is approximately 20 times the average field as measured using conventional macroscopic electrodes. This result casts serious doubt on the existing macroscopic matrix theories involving classical piezoelectricity.

Corrosion of Titanium

Commercially pure titanium and Ti-6Al-4V specimens have been studied using potentiostatic corrosion testing, differential capacitance, electron optics and Auger spectroscopy in order to better understand the way titanium behaves as an implant material. A closed corrosion cell, previously developed at the LRSM, was used to stimulate important aspects of the body environment. The results indicate that under all pH, O_2 , and amino acid ranges studied, Ti is a superior metal for implantation as measured in static corrosion testing. It is now important that testing under dynamic conditions, such as cyclic stress, and abrasion, be conducted since these more closely simulate the actual state of the titanium implant in function.

Dental Implants

Titanium blade-vent implants were implanted in the mandibles of Beagle dogs and were either subjected to functional loading or were not. Specimens were studied after 2 months, 4 months, 6 months, and one year of implantation. The formation of a dense fibrous capsule was clearly noted in all cases involving function of the implant. The structure of this capsule and surrounding tissue is currently being investigated. It appears that relative motion between the implant and the tissue always leads to the formation of soft tissue (fibrous capsule). This is being investigated further.

Publications:

Koh, J. K., Steinberg, M. E., Korostoff, E. and Pollack, S. R., "Changes in Electrical and Mechanical Properties of Whole Bone Related to Maturation", *Surgical Forum* 26, (1975) (Accepted)

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Pollack, S. R., "The Viscoelastic Properties of Human Dentin", *J. Biomed. Mater. Res.* 9, 661 (1975)

Pollack, S. R., Sutow, E. and Korostoff, E., "In Vitro Corrosion and Capacitive Behavior of 316-L Stainless Steel", *J. Biomed. Mater. Res.* (Accepted)

V. THE CENTRAL FACILITIES

Of central importance to the LRSM program in the materials sciences is the operation and maintenance of the central research facilities. Each has a faculty advisor, and all but three have full-time professional laboratory supervisors. Five of the facilities have additional permanent staff.

The general philosophy of operation is that the supervisors are not to provide service on demand. They are to maintain the facility and give instruction in its use, so that the students, post-doctoral fellows, and sometimes even the faculty can carry out the necessary operations. However, the supervisors often do get directly involved in the research activities of the MRL program, and many have appeared as co-authors of resulting publications. In addition, several patent applications have resulted from innovations generated within the LRSM Central Facilities.

It is difficult to overestimate the importance of these facilities for the LRSM research program. Almost all of the experimental work is directly dependent upon one or more of them, and to provide and maintain equipment and personnel on the scale required would be virtually impossible under a system of individual grants and contracts.

Mechanical Testing

Faculty Advisor: Prof. Charles J. McMahon, Jr.
Laboratory Supervisor: R. de la Veaux

This facility has now been consolidated in one area, and includes facilities for fatigue, creep, and general mechanical testing. The policy in setting up the facility has been to obtain the most versatile and flexible machinery, and to equip it with a wide range of accessories to permit easy interchange of function. Thus, the fatigue laboratory contains two channels of closed-loop electrohydraulic testing equipment usable on seven load frames ranging in capacity from 250 lbs. to 50,000 lbs. One frame is equipped with a high temperature, high vacuum chamber, for both resistance and induction heating to 1450°C. An analog computer can be used in the command mode in either channel. Recording equipment comprises x-y recorders, oscilloscopes, Brush recorders, and a punched tape/teleprinter system. A digital computer has been installed to carry out the functions of command, closing the loop and acquiring data, all with improved speed and accuracy. The facility is acquiring highly sensitive capacitance transducer system to detect

microstrains as small as 200 \AA at frequencies up to 200 Hz. Virtually any kind of mechanical test can be carried out from fracture mechanics to fatigue at 200 Hz. The creep laboratory has four Satec systems with instrumentation, vacuum systems and furnaces which permit complex creep and stress relaxation work up to 6,000 lbs. and 2200°F . A punched tape/teleprinter system has been added for data reduction. The general laboratory contains four Instron machines with a complete range of accessories, including high and low temperature equipment.

This facility is central to the scope and excellence of our present research effort in materials failure. It provides the equipment for all aspects of the program: cyclic-stress strain, creep-rupture, embrittlement, fatigue fracture, high temperature deformation of metal alloys, and deformation studies of polymers and amorphous alloys.

Organic Materials Preparation-Analytical Chemistry

Faculty Advisors: Prof. Robin M. Hochstrasser

Prof. David R. Gaskell

Laboratory Supervisor: Dr. A. R. McGhie

Deputy Supervisor: M. R. Kresz

Most aspects of inorganic analysis, with particular emphasis on trace level determinations, are provided by this facility, including atomic absorption, emission spectroscopy, gas chromatography, ultraviolet and visible absorption spectroscopy, scintillation and geiger counting, differential pulse polarography and a variety of electroanalytical techniques. For organic materials analysis we have, in addition to those listed above, analytical high pressure liquid chromatography and thin layer chromatography. Approximately 60% of the analytical work load involves routine measurements for characterizing reagent purity and contamination levels in starting materials and for establishing the composition of in-process and finished specimens. The remaining 40% of the effort is devoted to devising new procedures for solving specific analytical problems.

The facility's principal functions in organic materials preparation are separation/purification, and the growth of pure and doped single crystals. Equipment and techniques available include distillation, sublimation, preparative gas chromatography, thin layer and high pressure liquid chromatography, zone refining and crystal growth from the melt, vapor and solution. In addition a small effort in organic synthesis is maintained for materials which are not commercially available.

A major part of the effort in organic materials preparation is in devising methods for producing the ultrapure materials required for the studies of the optical, electrical and magnetic properties of organic

crystals and charge transfer compounds being conducted by our research group in the molecular crystals area.

X-Ray Diffraction

Faculty Advisor: Prof. Jerry Donohue

Laboratory Supervisor: H. Katz

The X-ray diffraction facility is equipped for crystal and molecular structure determinations using single crystal and powder techniques, identification of materials, crystal orientation and perfection measurements, elemental analysis by fluorescence, small angle scattering and temperature dependent phase change studies. The major equipment in the facility includes a Picker four-circle single-crystal diffractometer with a PDP-8 computer control unit; a Philips and a General Electric diffractometer, each with lithium fluoride monochromator; a vacuum fluorescence unit; a single crystal orienter; a scanning digital microdensitometer; a high temperature diffractometer attachment; a small angle scattering unit; a rotating anode x-ray unit in a cold room; and a variety of cameras for single crystal, powder and back reflection measurements.

Because all research groups in the program are concerned with the relationship between the structure of a material and its properties, the facility is involved in a wide variety of research problems. Prominent among these are complete x-ray crystal structure determinations of both organic and inorganic crystals of interest to the molecular crystals, electronic and magnetic materials, and biomaterials groups. Researchers in the area of materials failure use the x-ray facility for studies of the temperature dependence of long range order in alloys and of the topography of alloy surfaces as related to mechanical properties. Measurements of crystal orientation for optical and magnetic measurements and examination of thin films for crystal perfection are carried out routinely.

Spectroscopy

Faculty Advisor: Prof. Eugene R. Nixon

The facility is equipped for most kinds of optical measurements over the frequency range from vacuum ultraviolet to far infrared. Studies in emission, absorption, reflection, Raman scattering and Brillouin scattering are all being carried out on a variety of prism, grating and interferometric spectrometers. Research groups from Chemistry, Electrical Engineering, Metallurgy and Physics use the facility periodically in projects dealing with optical properties of organic crystals, charge-transfer compounds, thin films and surface properties, graphite compounds, and semiconductor materials.

Electron Microscopy-Metallography-Photography

Faculty Advisor: Dr. Campbell Laird
Laboratory Supervisor: R. G. White
Research Specialist: A. M. Lindemanis
Laboratory Assistants: A. Vaskelis
D. Townsley

The major equipment in this facility includes a Philips EM 300 transmission electron microscope, a Philips AMR Mark III electron microprobe, a Philips PSEM 500 scanning electron microscope and a JEOL JSM-U3 scanning electron microscope equipped with an EDAX energy dispersive x-ray spectrometer of better than 200 eV resolution. The Philips EM 300 and the JEOL JSM-U3 with the EDAX x-ray spectrometer are equipped so that images and x-ray data can be stored on a centrally located video tape deck. A PDP 11 computer is being installed which will provide "on-line" data processing for the EDAX spectrometer and the microprobe. Ancillary equipment includes an ion micromilling instrument, vacuum evaporator, ultra-microtome, laser facility, and optical microscopes. The major use of the facility has been on research projects in materials failure, chemical metallurgy, electronic materials, organic and inorganic conductors, and biomaterials. In the past year over 107 different researchers amassed a total of nearly 2170 hours of equipment use time. This is one of our most widely used facilities.

The metallography section of this facility provides services for materials failure studies. It includes equipment for specimen sectioning, mounting, grinding, lapping and polishing, and metallographic microscopes equipped for photomicrography. Several hardness and micro-hardness testers are also located in the center.

The photography section contains equipment for film and print processing and enlarging for photomicrographs and other forms of data recorded photographically. There are also provisions for slide-making.

Magnetic Field

Faculty Advisor: Prof. Charles D. Graham, Jr.
Laboratory Supervisor: P. J. Flanders
Laboratory Assistant: L. Cheskis

The High-Field Magnet Laboratory comprises a 6 megawatt motor-generator set, a heat exchange system capable of dissipating 4 megawatts continuously, and 4 Bitter-type water-cooled solenoids ranging from a 1-inch bore, 135 kOe to a 5-inch, 60 kOe magnet with radial access ports.

Two magnet stations permit preparation for new experiments to proceed simultaneously with magnet operation. The Laboratory also operates six electromagnets, ranging in size from 12-inch to 2-inch pole diameter and equipped with a variety of magnetic measuring equipment. The magnet facility is one of four comparable installations in the United States.

Instrumentation

Faculty Advisor: Prof. John E. Fischer
Laboratory Supervisor: S. Macri
Laboratory Assistant: F. Hellmig, Jr.

This laboratory performs a number of the inter-related and specialized functions. Its main functions are: (1) the standardization and calibration of all types of electronic equipment and laboratory apparatus; (2) the design of specialized instrumentation for other laboratories; and (3) to provide a pool of general purpose instruments for short term use by members of the LRSM.

The electrical standards lab is currently equipped for a number of precision calibrating services. Calibrations are all traceable to the National Bureau of Standards. The laboratory has also within its facility transportable equipment to compare laboratory standards with NBS.

Measurement capabilities are in the following areas: DC voltage, covering the full range of potential measurements from one microvolt up to 50,000 volts; DC current, covering the full range of current measurements from one picoampere up to 50 amperes; AC voltage and current covering all frequencies up to 100 megahertz. The range of measurements in this area is from 10 microvolts up to 1500 volts, and currents up to 20 amperes.

Other areas of measurements include: Resistance, 10^{-6} to 1 ohm with a current capacity of 10 amperes or less through sample - 1 ohm to 10^8 ohms - 10^5 to 10^{15} ohms applied voltage of 10 VDC; low temperature voltage and resistance measurements, covering a range from 30 microvolts to 3 picovolts resistance from 3×10^{-4} to 3×10^{-11} ohms at temperatures of 4.5 Kelvin or lower; frequency, covering the range from below one hertz up to gigahertz; capacitance, 2 and 3 terminal measurement covering the range of 10^{-17} to .11 farad; inductance range 1 microhenry to 1100 h. Other areas of measurements are: time, wave analysis and distortion measurements.

The facility has temperature measurement capabilities covering a range from -269°C (4.2 K) to 1450°C . Instrumentation capabilities

are: a temperature regulated furnace for thermocouple calibration having a temperature range capability from 30°C to 1205°C; also a calibrated standard is available having a range of 800°C to 2300°C for the calibration of radiation pyrometers. The facility is also able to calibrate vacuum gauges.

Materials Processing

Faculty Advisor: Prof. David P. Pope
 Laboratory Supervisor: W. J. Romanow
 Laboratory Assistants: G. Wood
 L. Cheskis

The Materials Processing Facility is comprised of five integrated laboratories; thin film deposition, melting, mechanical working, heat treating and materials preparation. Its function is to supply high quality materials for experimental study throughout the program.

The thin film deposition laboratory has facilities for making thin films of either single or co-evaporated materials by resistance heated sources or by evaporation with a Varian 2 kw e-gun. Substrate heating, cooling or pre-evaporation cleaning (by glow discharge) are available. The melting laboratory has facilities for both single crystal growing and vacuum induction melting. There is equipment for growing crystals by a number of different techniques. The mechanical working laboratory has facilities which include rolling mills, rotary swagers, and wire-drawing dies. The heat treating laboratory has equipment and facilities for the thermal treatment of materials over a wide range of temperatures and atmospheres. Included are tube furnaces, salt pot furnaces, air furnaces, muffle furnace and atmosphere furnaces with inert, oxidizing, reducing or evacuated ambients. Two Brew high temperature high vacuum furnaces are available for temperatures up to 3000°C. The materials preparation laboratory has provisions for powder preparation, particle sizing, materials handling and crystal cutting.

In addition to a wide range of metals and alloys, samples of oxides, halides, sulfides, and other compounds are prepared for work in all of the thrust areas except molecular solids.

Integrated Circuit and Semiconductor Facility

Faculty Advisor: Prof. Jay N. Zemel
 Laboratory Supervisor: T. J. Carroll

The Integrated Circuit and Semiconductor Facility (ICS) provides the basic processing and preparation equipment for both fundamental and applied studies of electronic materials.

The facility includes several types of epitaxial reactors for preparation of silicon (including in situ capability for chemical vapor deposition of silicon dioxide), IV-VI and II-VI semiconductors; vacuum evaporation systems for substrate metallization and/or other coatings; diffusion and oxidation furnaces; photolithographic equipment including photoresist spinners and developers, mask aligners and a coordinatograph for rubylith cutting; ultrapure handling systems including ultrapure water baths, dry boxes for handling materials under inert atmospheres and laminar flow hoods; bonding equipment including thermocompression, ultrasonic and welding gear; measurement facilities for characterizing devices and materials used for devices.

An ion implantation apparatus is presently being assembled which will provide a powerful tool for study of changes and control of the properties of electronic materials.

To properly house much of the above equipment a clean room facility providing Class 100 work stations is now being designed.

The ICS facility is used in the electronic materials program. Major efforts which use the facility include the study of PbS/Si heterojunctions, modulation spectroscopy, intercalated graphite compounds, surface wave phenomena and the study of IV-VI materials. Fabrication of microstructures of various types have been undertaken as well. The facilities are generally available to non-project users from outside LRSM, both from the University and elsewhere, on the same basis as to members of LRSM.

This is a new facility in the LRSM which receives only partial support; the remainder coming from contracts, grants and departmental resources.

Surfaces

Faculty Advisor: Prof. E. Ward Plummer

Laboratory Supervisor: Dr. H. C. Feng

This facility has two general purpose ultra high vacuum systems, thin film analyzer (TFA) and scanning Auger microprobe (SAM), for a variety of studies on solid surfaces and interfaces. Both the TFA and the SAM are equipped with fracture unit and can provide an elemental analysis as well as a depth profile of a specimen. The SAM, with a few microns lateral resolution, is capable of analyzing selected spot on the specimen. It can also provide an absorbed current micrograph and an Auger image of the surface analyzed.

The Surface Central Facility serves an ultra high vacuum consulting service for the LRSM, as well as furnishing basic surface instrumentation on a loan basis, such as residual gas analyzers, LEED optics, sputter guns, etc.

Data Processing Center

Faculty Advisor: Prof. Donald H. Voet

This facility consists of a PDP8/I computer with 8K-word memory, 32K-word magnetic disk storage, high-speed paper tape reader and punch, and teletype input-output, plus keypunches and an electronic desk calculator. It was established to accommodate the variety of small to medium computing problems generated throughout our materials science program. A large number of students and faculty employ the facility regularly for data reduction, curve fitting, program debugging, and similar jobs. The equipment is also used for the transfer of data from punched tape to punched cards for use on the University IBM 370 facility. A scanning microdensitometer, connected on-line to the PDP8/I computer, is used for analyzing x-ray diffraction data recorded on photographic films.

Photoelectron Spectroscopy

Faculty Advisor: Prof. E. Ward Plummer
Technician: L. Kovnat

This central facility is equipped with a high resolution (0.012 eV) photoelectron spectrometer capable of studying both gas phase and condensed phase material (at low temperature). The photon energies which are available are the resonance lines of He and Ne. Plans are under way to enhance the capability of this Facility to include ESCA for use with both gas phase and solid state materials.

Mass Spectrometry

Faculty Advisor: Prof. John G. Miller

The use of mass spectroscopy has become increasingly important to a variety of LRSM researchers within the last year. As a result, the Mass Spectrometry Facility is being upgraded considerably. The facility currently consists of a CEC Type 21-130 Mass Spectrometer which has been modified to increase the mass range and has been equipped with a peak-height ratio module and recorder for determining isotope compositions.

This instrument has proven inadequate for many users and, as a result, LRSM in cooperation with the Chemistry Department has employed a full-time specialist in mass spectroscopy in order to improve the facility. The primary function of this specialist will be to maintain and run the Perkin-Elmer RMH-2 High Resolution Mass Spectrometer located in the chemistry department. This machine should now routinely provide both high and low resolution spectra.

VI. LRSM ACADEMIC STAFF

- Belton, Geoffrey R. , Professor of Metallurgy and Materials Science
- Brennen, William R. , Associate Professor of Chemistry
- Brown, Norman, Professor of Metallurgy and Materials Science
- Burstein, Elias, Professor of Physics
- Caspari, Max E. , Professor of Physics
- Cava, Michael P. , Professor of Chemistry
- Chang, Mark S. , Assistant Professor of Electrical Engineering and Science
- Donohue, Jerry, Rhodes-Thompson Professor of Chemistry
- Egami, Takeshi, Assistant Professor of Metallurgy and Materials Science
- Fischer, John E. , Associate Professor of Electrical Engineering and Science
- Fitts, Donald D. , Professor of Chemistry
- Forsman, William C. , Associate Professor of Chemical and Biochemical Engineering
- Garito, Anthony F. , Associate Professor of Physics
- Gaskell, David R. , Associate Professor of Metallurgy and Materials Science
- Girifalco, Louis A. , Professor of Metallurgy and Materials Science and Associate Dean for Graduate Studies and Research, College of Engineering and Applied Science
- Graham, Charles D. , Jr. , Professor of Metallurgy and Materials Science
- Graham, William R. , Associate Professor of Metallurgy and Materials Science
- Gray, Harry J. , Jr. , Professor of Electrical Engineering and Science
- Gustafsson, Torgny, Assistant Professor of Physics
- Hameka, Hendrik F. , Professor of Chemistry
- Harris, A. Brooks, Professor of Physics
- Heeger, Alan J. , Professor of Physics and Director of the Laboratory for Research on the Structure of Matter
- Hochstrasser, Robin M. , Blanchard Professor of Chemistry
- Laird, Campbell, Professor and Chairman of Metallurgy and Materials Science

Langenberg, Donald N. , Professor of Physics and Vice Provost for
Graduate Studies and Research

Lubensky, Tom C. , Associate Professor of Physics

MacDiarmid, Alan G. , Professor of Chemistry

Maddin, Robert, University Professor of Metallurgy and Materials Science

McMahon, Charles J. , Jr. , Professor of Metallurgy and Materials Science

Myers, Alan L. , Professor of Chemical and Biochemical Engineering

Nixon, Eugene R. , Professor of Chemistry

Plummer, E. Ward, Associate Professor of Physics

Pope, David P. , Associate Professor of Metallurgy and Materials Science

Rabii, Sohrab, Associate Professor of Electrical Engineering and Science

Schrieffer, J. Robert, Mary Amanda Wood Professor of Physics

Smith, Amos B. , III, Assistant Professor of Chemistry

Sneddon, Larry G. , Assistant Professor of Chemistry

Soven, Paul, Associate Professor of Physics

Thompson, Thomas E. , Assistant Professor of Electrical Engineering
and Science

Topp, Michael R. , Assistant Professor of Chemistry

Voet, Donald H. , Associate Professor of Chemistry

Wayland, Bradford B. , Professor of Chemistry

Worrell, Wayne L. , Professor of Metallurgy and Materials Science

Zemel, Jay N. , RCA Professor of Solid State Electronics and Chairman
of Electrical Engineering and Science

LRSB AFFILIATED FACULTY

Callen, Herbert B. , Professor of Physics

Korostoff, Edward, Professor of Biomaterials in Dental Medicine and
Metallurgy and Materials Science

Miller, John G. , Professor of Chemistry

Pollack, Solomon R. , Professor of Metallurgy and Materials Science

White, David, Professor and Chairman of Chemistry

VII. DEGREES GRANTED

Doctor of Philosophy Degrees Conferred
in the Materials Sciences
August 1975 to May 1976

- Abd-Elmageed, Mervat E. (Chemistry). "ESR Probing for the Nature of Phosphines σ -Donor Orbitals: Cobalt II Complexes of Trivalent Phosphorus Ligands". Thesis Director: Dr. B. B. Wayland
- Aymeloglu, Simeon (Electrical Engineering and Science). "Low Temperature Admittance Studies in N-Channel Si MOSFET's". Thesis Director: Dr. J. N. Zemel
- Baumann, Lawrence S. (Physics). "Self-Consistent Treatment of the Anderson Model of Dilute Magnetic Alloys". Thesis Director: Dr. P. E. Bloomfield
- Bellafiore, Dennis J. (Physics). "Gamma-Gamma Perturbed Angular Correlation Investigation of the Hyperfine Interactions for $^{154}\text{Gd}^{3+}$ in GdAlG, GdIG, YAlG, and YIG as a Function of Temperature and Applied Magnetic Field". Thesis Director: Dr. M. E. Caspari
- Buchner, Stephen P. B. (Physics). "Resonance-Enhanced Allowed, Field-Induced and Wave-Vector-Dependent Raman Scattering from the Surface Region of InAs". Thesis Director: Prof. E. Burstein
- Bykovetz, Nicholas (Physics). "Impurity Magnetization Studies in Europium Chalcogenides". Thesis Director: Dr. M. E. Caspari
- Chi, Cheng-Chung J. (Physics). "Microwave Response of Nonequilibrium Superconductors". Thesis Director: Dr. D. N. Langenberg
- Chu, Chih J. (Chemistry). "Structure and Properties of cis-dichloro-siliconium bis(bipyridylide)". Thesis Director: Dr. A. G. MacDiarmid
- Cohen, Marshall J. (Physics). "The Peierls Instability in Quasi-One Dimensional Metals". Thesis Director: Dr. A. J. Heeger
- Coleman, Lawrence B. (Physics). "DC and Far Infrared Conductivity and Associated Materials Studies of (TTF)(TCNQ)". Thesis Director: Dr. A. J. Heeger
- Davis, John J. (Chemistry). "Photochemistry of t-Butyl Perlaurate". Thesis Director: Dr. J. G. Miller

- DeLuccia, John J. (Metallurgy and Materials Science). "Electrolytic Hydrogen in Beta Titanium". Thesis Director: Dr. G. R. Belton
- Doane, Daryl A. (Metallurgy and Materials Science). "Magnetoelastic Interactions in SmCo_5 ". Thesis Director: Dr. C. D. Graham, Jr.
- Friedman, Joel M. (Chemistry). "Theoretical and Experimental Aspects of Resonant Light Scattering". Thesis Director: Dr. R. M. Hochstrasser
- Kapur, Vijay K. (Chemistry). "Magnetic Resonance Studies of Paramagnetic Transition Metal Complexes". Thesis Director: Dr. B. B. Wayland
- Kozub, Stephen G. (Chemistry). "Kinetics and Mechanisms of the Bromate Oxidations of Substitution-Inert Iron(II) Complexes in Acidic Aqueous Solution". Thesis Director: Dr. J. P. Birk
- Madden, William G. (Chemistry). "The Structure of Simple Fluids". Thesis Director: Dr. D. D. Fitts
- Mehne, Larry F. (Chemistry). "Axial Effects in Planar Complexes: Iron Tetraphenylporphyrin and Nickel Bisdiphenylglyoxime Halides". Thesis Director: Dr. B. B. Wayland
- Minka, Charles J. (Chemical and Biochemical Engineering). "Thermodynamic Studies of Adsorption from Vapor and Liquid Mixtures on Solids". Thesis Director: Dr. A. L. Myers
- Mirandy, Louis P. (Mechanical Engineering and Applied Mechanics). "Brittle Fracture under Multiaxial Loading Conditions". Thesis Director: Dr. B. Paul
- Price, Jerold H. (Chemistry). "Properties and Reactions of Alkyl Sulfoxide Complexes of Palladium(II) and Platinum(II)". Thesis Director: Dr. B. B. Wayland
- Ritter, Thomas A. (Metallurgy and Materials Science). "Strain-Related Potentials in Human and Bovine Bone". Thesis Director: Dr. E. Korostoff
- Sain, Djordjije R., (Metallurgy and Materials Science). "Interfacial Reaction Kinetics in the Decarburization of Liquid Iron by Carbon Dioxide". Thesis Director: Dr. G. R. Belton
- Shieh, Huey-Sheng (Chemistry). "Structural Studies of the Molecular Complexes of Biological Interest". Thesis Director: Dr. D. H. Voet

Sood, Ashok (Metallurgy and Materials Science). "Growth and Properties of Metastable Pseudobinary Alloy Films of $Pb_{1-x}Cd_xS$ ". Thesis Director: Dr. J. N. Zemel

Weber, David C. (Chemistry). "Stabilization of Non-Classical Silicon Ions by 2,2'-Dipyridyl Radical Anions and Dianions". Thesis Director: Dr. A. G. MacDiarmid

Welsh, William J. (Chemistry). "Theoretical Studies in Surface Phenomena". Thesis Director: Dr. D. D. Fitts

Yang, Cary Y-W. (Electrical Engineering and Science). "Relativistic Scattered-Wave Method and Its Applications to Molecules and Clusters in Solids". Thesis Director: Dr. S. Rabii

Yeh, James T.-C. (Physics). "Characteristics of Very Small Josephson Tunnel Junctions". Thesis Director: Dr. D. N. Langenberg

Young, Jing-Jue (Electrical Engineering and Science). "Kinetics of Ambient Gas Effect on Thin PbSe Epitaxial Films". Thesis Director: Dr. J. N. Zemel

Destinations of Graduates
August 1975 to May 1976

Abd-Elmageed, Mervat E. , Postdoctoral, California Institute of Technology

Aymeloglu, Simeon, Senior Engineer, I. T. T.

Baumann, Lawrence S. , Research Scientist, Control Data Corporation

Bellafiore, Dennis J. , Postdoctoral, University of Pennsylvania

Buchner, Stephen P. B. , Postdoctoral, University of Maryland

Bykovetz, Nicholas, Position pending

Chi, Cheng-Chung J. , Postdoctoral, University of California at Berkeley

Chu, Chih J. , No placement at present

Cohen, Marshall J. , Postdoctoral, University of Pennsylvania

Coleman, Lawrence B. , Assistant Professor, University of California
at Davis

Davis, John J. , Chemist, AMCHEM, Division of Union Carbide

DeLuccia, John J. , Branch Head, Materials Protection Branch, U. S.
Naval Air Development Center

Doane, Daryl A. , Member, Research Staff, RCA Laboratories

Friedman, Joel M. , Postdoctoral, Bell Telephone Laboratories

Kapur, Vijay K. , Visiting Scientist, Stanford Research Institute

Kozub, Stephen G. , Coordinator of Chemistry Labs. , University of
Pennsylvania

Madden, William G. , Postdoctoral, University of Chicago

Mehne, Larry F. , Assistant Professor, Covenant College

Minka, Charles J. , Assistant Professor, University of Yaoundé E. N. S.
Polytechnique, Camaroon

Mirandy, Louis P., Dynamics Engineer, Boeing Vertol Company

Price, Jerold H., Assistant Professor, Community College of Philadelphia

Ritter, Thomas A., Research Engineer, Davis & Geck

Sain, Djordjije R., Postdoctoral, Pennsylvania State University

Shieh, Huey-Sheng, Postdoctoral, University of Michigan

Sood, Ashok, Staff Scientist, Mobil Tyco Solar Energy Corporation

Weber, David C., Resident Research Associate, Naval Research Laboratories

Welsh, William J., Research Scientist, Proctor and Gamble

Yang, Cary Y-W., Postdoctoral, Massachusetts Institute of Technology

Yeh, James T-C., Postdoctoral, Cornell University

Young, Jing-Jue, Engineer, RCA

Destinations of Post-doctoral Fellows
August 1975 to May 1976

Ahearn, John S. , Senior Research Scientist, Martin-Marietta Company

Banerji, Samir K. , Senior Research Metallurgist, Foote Mineral
Company

Bray, Robert G. , Research Chemist, Allied Chemical Company

Briant, Clyde L. , Staff Scientist, General Electric

Dagaev, Nikolai L. , Associate Professor, Novosibirsk Institute of
Electrical Engineering

Holcomb, W. K. , Assistant Professor, University of Alabama

Kuramoto, Eiichi, Associate Professor, Kyushu University

Lederman, F. , Member of Staff, General Electric

Liebsch, Ansgar, Research Staff Member, Institut F. Festkorperphysik
Julich, W. Germany

Mikulski, Chester M. , Assistant Professor, Beaver College

Russo, Peter J. , Teaching Staff, Philadelphia General Hospital

Saran, Mohan S. , Researcher, Hooker Chemical Company

Sasa, Tadashi, Research Associate, University of Tokyo

Talaat, Hassan, Faculty Position, University of Cairo

Ucisik, Ahmet H. , Research Associate, T. C. Istanbul Teknik Universitesi

VIII. PUBLICATIONS

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- Aymeloglu, S. and Zemel, J. N., "Freeze-Out Effects on n-Channel MOSFET's", IEEE Trans. on Electron Devices ED-23, 466 (1976)
- Bellafiore, D. J., "PAC Attenuation Coefficients G_{22} and G_{44} for a Randomly Oriented Non-Axially Symmetric Static Electric Quadrupole Interaction for the Intermediate Spin $I = 2$ ", Hyperfine Interactions (Accepted)
- Belsky, V. K. and Voet, D., "Tetracarbomethoxytetrathiofulvalene", Acta Cryst. B32, 272 (1976)
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- Buckner, S. A. and Langenberg, D. N., "Riedel Singularity in Tin-Tin Oxide-Tin Tunnel Junctions", *J. Low Temp. Phys.* 22, 569 (1976)
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- Chang, M. S., "Acousto-Optic Filters" *IEEE Circuits and Systems* 10, (1976)
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- Chen, W. P., Chen, Y. J. and Burstein, E., "The Surface EM Modes of a Surface Quantized Plasma Layer on a Semiconductor Surface", *Proc. Int. Conf. on Electronic Properties of Quasi-Two Dimensional Systems* (in press)
- Chiang, C. K., Cohen, M. J., Garito, A. F., Heeger, A. J., Mikulski, C. M. and MacDiarmid, A. G., "Electrical Conductivity of (SN)_x", *Solid State Commun.* 18, 1451 (1976)
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- Egami, T. and Brooks, M. S. S., "Theory of Collective Excitation in Strong Crystal Fields. II. Application to S=1 Singlet Ground State Ferromagnet", Phys. Rev. B12, 1029 (1975)
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- Forsman, W. C. with Gupta, S. K. and Kumar, A., "A Generalized Treatment of Segment Densities in Linear and Branched Random-Flight Chains", Chem. Phys. Lett. (in press)
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- Friedman, J. M. and Hochstrasser, R. M., "The Use of Fluorescence Quenchers in Resonance Raman Spectroscopy", Chem. Phys. Letts. 33, 225 (1975)
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IX. LRSM SEMINAR PROGRAM

Dr. A. Aharony, Bell Telephone Laboratories and Tel-Aviv University,
Israel

"Is the Critical Behavior of Magnets Universal?"

Dr. T. Anantharaman, Banaras Hindu University, Varanasi, India

"The Metallography of Splat-Cooled Metals"

Dr. J. Applebaum, Bell Telephone Laboratories

"A Theoretical Study of Surface Bonding - Si and GaAs(100) -
Surface Dimerization, Tetramerization!?"

Prof. M. F. Ashby, University of Cambridge

"Case Studies in the Use of Deformation Mechanism Maps"

Dr. R. H. Baughman, Allied Chemical Corporation

"Polymer Crystals with Quasi One-Dimensional Electron
Delocalization"

Prof. R. Bersohn, Columbia University

"Photodissociation of Molecular Beams"

Prof. J. M. Blakeley, Cornell University

"Segregation at Transition Metal Surfaces"

Dr. R. G. Bray, Department of Chemistry, University of Pennsylvania

"Dye Laser Spectroscopy of Molecules Resulting from the
Simultaneous Absorption of Two or More Photons"

Dr. L. Brus, Bell Telephone Laboratories

"Photophysics of Bound and Dissociative Molecular States of Rare
Gas Lattices"

Prof. P. Chaikin, University of California at Los Angeles

"Phonon Structure in the Tunneling Characteristics of Proximity
Effect Sandwiches"

Prof. M. S. Chang, Department of Electrical Engineering and Science,
University of Pennsylvania

"Acousto-Optic Filters"

Dr. E. Conwell, Xerox Corporation

"Surface Plasmons Guided Waves and Integrated Optics"

- Prof. H. E. Cook, University of Illinois at Urbana-Champaign
"Pre-Transition and Nucleation Phenomena in Structural Phase Transformations"
- Dr. P. S. Corden, United States Arms Control and Disarmament Agency
"Technology and Weapons of Mass Destruction -- The Turn of the Screwdriver"
- Mr. J. H. Crate, Dupont Company
"Current Trends in Plastic Design"
- Dr. H. Dalal, SKF Industries
"The Role of Material Science in Roller Bearing Technology"
- Dr. F. Damara, Special Metals Corporation
"Vacuum Melting, A Case History in Industrial Innovation"
- Dr. D. C. Doetschman, State University of New York, Binghamton
"Electron Spin Echo and Laser Photolysis Experiments on Molecular Triplet States"
- Prof. H. Ehrenreich, Visiting Professor of Physics, University of Pennsylvania; Harvard University
"Why are d- Electron Metals Interesting? "
- Dr. R. J. Elliott, Oxford University, England
"Phase Transitions in Spin-Phonon Coupled Systems"
- Dr. D. Emin, Sandia Laboratories
"A Qualitative Discussion of Small Polaron Formation and Motion"
- Dr. B. Eyre, Atomic Energy Research Establishment, Harwell, England
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"Electrons on the Surface of Helium"

KEY TO ABBREVIATIONS

AFML	Air Force Materials Laboratory
AFOSR	Air Force Office of Scientific Research
AISI	American Iron and Steel Institute
ARO	Army Research Office
ARO-D	Army Research Office-Durham
ARPA	Advanced Research Projects Agency
EPRI	Electric Power Research Institute
ERDA	Energy Research and Development Administration
IBM	International Business Machines Corporation
IREX	International Research and Exchanges Board
JPL	Jet Propulsion Laboratory
KCC	Kennecott Copper Corporation
LRSM	Laboratory for Research on the Structure of Matter
MERADCOM	Materials Engineering Research and Development Center
MPC	Metal Properties Council
NASC	Naval Air Systems Command
NATO	North Atlantic Treaty Organization
NIDR	National Institute of Dental Research
NIH	National Institutes of Health
NSF	National Science Foundation
NSF/MRL	National Science Foundation/Materials Research Laboratory
NSF-RANN	National Science Foundation-Research Applied to National Needs
ONR	Office of Naval Research
PRF	Petroleum Research Fund
PSEF	Pennsylvania Science and Engineering Foundation
RC	Research Council
U of P	University of Pennsylvania
USA	United States Army

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